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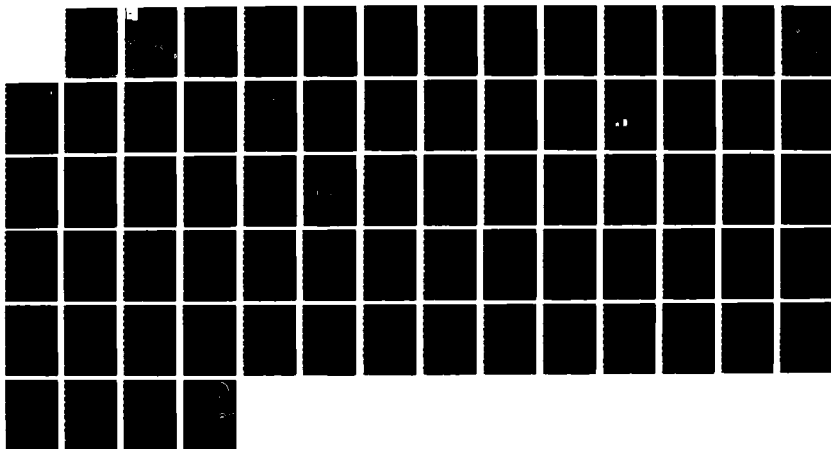
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# PRELIMINARY ASSESSMENT OF BIOACCUMULATION OF METALS AND ORGANIC CONTAMINANTS AT THE TIMES BEACH CONFINED DISPOSAL SITE, BUFFALO, N.Y.

by

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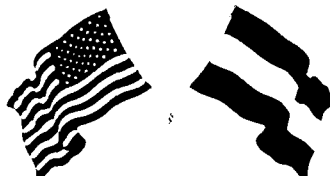
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DEPARTMENT OF THE ARMY

Waterways Experiment Station, Corps of Engineers  
PO Box 631, Vicksburg, Mississippi USA 39180-0631



WES  
TNO

April 1987

Final Report

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Memorandum of Understanding Concerning  
Dredging and Related Technology

Prepared for US Army Engineer District, Buffalo  
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19 ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>This document reports the results of preliminary investigations of contaminant mobility at the Times Beach confined disposal site in Buffalo, New York. A terrestrial earthworm (<i>Eisenia foetida</i>) bioassay procedure was applied in the field and in a laboratory controlled-environment chamber 7 years after terminating the disposal of dredged material. Native earthworms were collected from Times Beach and a nearby reference area, and native fishes were collected from the lake within Times Beach and from the mouth of the Buffalo River. Worm and fish tissues and the dredged material used in laboratory bioassays and in the field studies were analyzed for heavy metals, polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), and polynuclear aromatic hydrocarbons (PAHs).</p> <p>In the lake (approximately 50 percent of the site), mercury and PCB concentrations (fresh weight) in edible fish ranged from 0.1 to 0.6 <math>\mu\text{g}\cdot\text{g}^{-1}</math> and 0.3 to 1.1 <math>\mu\text{g}\cdot\text{g}^{-1}</math>.</p> <p style="text-align: right;">(Continued)</p>					
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Dredged material	Habitat development	Succession
Earthworm	HCB	Terrestrial
<i>Eisenia foetida</i>	Mercury	Wetland
Field verification	PAHs	
Fish	PCBs	
Food chain	Plant	

19. ABSTRACT (Continued).

respectively. In the wetland (approximately 25 percent of the site), no native earthworms or measurable numbers of other soil-dwelling macroinvertebrates were found. In the wooded upland (the remaining 25 percent of the site), cadmium concentrations in native earthworms ranged from 84 to 113  $\mu\text{g}\cdot\text{g}^{-1}$  (ash-free dry weight). Individual PCB congeners ranged from 0.05 to 0.9  $\mu\text{g}\cdot\text{g}^{-1}$  (ash-free dry weight). Concentrations of specific PAHs varied from less than 0.2 (e.g., anthracene and perylene) to more than 0.5  $\mu\text{g}\cdot\text{g}^{-1}$  (e.g., benzo(a)anthracene, benzo(a)pyrene, and benzo(g,h,i)perylene).

Experimental laboratory studies with the earthworms were conducted with materials collected along two transects that extended from the water's edge into the woodland. Metal concentrations in the wetland materials were higher than those from the upland areas. The uptake of cadmium, mercury, and arsenic by the earthworms was similar from both wetland and upland materials, which suggested that the bioavailability was lower in the wetland. The uptake of copper was proportional to the concentrations in the substrates, however. Thus, the bioavailability of copper apparently was similar in both wetland and upland materials. The concentrations of organic contaminants in the substrates and bioaccumulation in the earthworms were generally higher on wetland materials, which suggested that bioavailability of PCB components was similar in both environments. Bioavailability of PAHs was component-specific. For instance, the bioavailability of phenanthrene was greater in the upland, that of anthracene similar in both upland and wetland, and that of benzo(a)pyrene greater in the wetland.

Analyses of soil/dredged material samples from different depths suggested that the concentrations of contaminants have changed with time. The layer of dredged material below the water table remained unconsolidated and in a reduced condition. Contaminant concentrations in this layer were considered to be essentially the same as those in the original dredged material. The concentrations of some specific elements in the surface mineral layer may have increased (e.g., potassium, magnesium, titanium, vanadium, and cadmium) in comparison with those in the underlying unconsolidated dredged material. The concentrations of other elements either have remained essentially unchanged (e.g., sodium, cobalt, and lead) or have decreased (e.g., chlorine, chromium, copper, arsenic, and mercury) in the surface mineral layer. Some PAHs in the surface mineral layer decreased (anthracene and pyrene), whereas others remained essentially unchanged (benzo(a)pyrene and benzo(a)anthracene) from those in the underlying deep layer. Analyses of the surface leaf litter showed that cadmium concentrations were elevated in comparison with those in the underlying materials. These elevated cadmium levels appeared to be the result of plant uptake and subsequent enrichment of the forest floor by leaf fall. This also may explain the observed higher concentrations of some of the other elements in the surface mineral layer.

→ Although fishes and soil invertebrates at Times Beach are contaminated, it is unlikely that there would be any substantial adverse impact upon migratory species temporarily feeding in the area, as the overall size of Times Beach is very small. Frequent consumption of fishes caught within the site is not recommended, however.

## EXECUTIVE SUMMARY

A terrestrial animal bioassay procedure was applied to dredged material at the Times Beach confined disposal site, Buffalo, New York, 7 years after disposal was terminated. This procedure was applied both in the field and in the growth chamber. At the same time, native worms were collected from Times Beach and a nearby terrestrial reference area. Native fishes were collected from the small lake within Times Beach and from an aquatic reference area. Worm and fish tissues and the dredged material to which the worms were exposed were analyzed for heavy metals, polychlorinated biphenyls (PCBs), hexachlorobenzene, and polynuclear aromatic hydrocarbons (PAHs). Bioavailability of the contaminants differed considerably throughout the site. In the small lake (approximately 50 percent of the site), mercury and PCB concentrations although high were within the range of concentrations allowed in fish taken by local fisheries for human consumption. In the wetland (approximately 25 percent of the site), some uptake of all contaminants occurred in the experimental worms. No native earthworms or other quantitative amounts of soil-dwelling invertebrates were found in this area, however. Thus, this problem is only a potential one that is expected to diminish in time with further consolidation. In the wooded upland (the remaining 25 percent of the site), the major potential problems are the rather high concentrations of cadmium that were encountered in the native earthworms and the occurrence of moderate levels of PCBs and PAHs.

The experimental work with the worms suggested that the woodland is still in a successional stage. It is expected that bioavailability of most heavy metals, PCBs, and some PAH components will decrease in time. Bioavailability of cadmium, however, seems to increase with time through enrichment of the forest floor by leaf fall.

From an environmental point of view for the site as a whole, each habitat within the site is regarded as too small to contain a considerable wildlife population with lifetime exposure. Animals feeding throughout the site will be exposed to a strongly divided risk due to the large differences in contaminant bioavailability within the different habitats. Local fisheries for human consumption are advised to be restricted.

## PREFACE

This report summarizes the first results of joint American-Dutch research conducted under the auspices of the United States-The Netherlands Memorandum of Understanding Concerning Dredging and Related Technology. With reference to sediments and dredged material, these bioassay techniques were developed, applied, and evaluated by the US Army Engineer Waterways Experiment Station (WES) and The Netherlands Organization for Applied Scientific Research (TNO), Division of Technology for Society (MT). Until recently, both the WES and MT-TNO independently developed and/or applied procedures based on the disposal strategies that were locally confronting their sponsors. From early 1983, these organizations have cooperated with joint research projects. In order to facilitate the maximum exchange of expertise, Dr. J. M. Marquenie of the Department of Biology, MT-TNO, was stationed at the WES from 7 July until 16 October 1983. He collaborated with Drs. John W. Simmers and Stratford H. Kay of the Ecosystem Research and Simulation Division (ERSD), Environmental Laboratory (EL), on three different projects. These projects were Times Beach, confined disposal site contaminant mobility studies at Buffalo, New York; Black Rock, Field Verification Program experimental upland and wetland creation disposal site studies at Bridgeport, Connecticut; Ottawa, area strip mine reclamation study site at Ottawa, Illinois. This joint report deals with the Times Beach contaminant mobility studies.

Financial support for these studies was supplied by the US Army Engineer District (USAED), Buffalo, and the WES, through the US Army Research Development and Standardization-United Kingdom (Contract DAJA 45-84-C-0015), the Netherlands Ministry of Transport and Public Works, and TNO.

General supervision was provided by Dr. J. S. A. Langerwerf, Head, Department of Biology, MT-TNO; Mr. Donald L. Robey, Chief, ERSD; and Dr. John Harrison, Chief, EL. Review, valuable suggestions, and constructive comments were made by Mr. R. P. Leonard, USAED, Buffalo; Dr. Charles R. Lee, WES; and Dr. Langerwerf, Mr. R. Henzen, and Ms. T. Adema, TNO. Support in analytical chemistry was provided by the following TNO personnel: Dr. H. Compaan (PCBs), Dr. H. Gielen (PAHs), Mr. P. De Jong (metals in tissues), and Mr. J. Spyk (metals in soils). Laboratory and field work was provided by the following: Messrs. R. G. Rhett, W. M. Brodie, W. Rayford, and D. K. Crawley of the WES, Messrs. R. P. Leonard and Len Bryniarski of the USAED, Buffalo; and

Mr. R. Henzen of TNO. Additional comments were received from members of the WES Animal Bioassay Working Group on 6-10 August 1984, including the following: Dr. N. Beyer, US Fish and Wildlife Service; Dr. G. Bryan, Marine Biological Association, United Kingdom; Dr. Clive Edwards, Rothamsted Experimental Station, United Kingdom; Dr. M. Ireland, University College of Wales, United Kingdom; Dr. M. Johnson, University of Liverpool, United Kingdom; Dr. R. H. D. Lambeck, Delta Institute for Hydrobiological Research, The Netherlands; Dr. E. Neuhauser, Cornell University; Dr. B. Pierce, Office, Chief of Engineers; Dr. F. Prosi, University of Heidelberg, Federal Republic of Germany; Dr. W. Stickle, Louisiana State University, Dr. B. Walton, Oak Ridge National Laboratory; Dr. G. Wilhelm, Morton Arboretum, Chicago, Illinois; Dr. B. Hunter, British Petroleum, United Kingdom; Mr. J. Mansky, USAED, New York; and Mr. N. Rubenstein, US Environmental Protection Agency. This report was edited by Ms. Lee T. Byrne of the Information Products Division, Information Technology Laboratory, WES.

COL Allen F. Grum, USA, was the previous Director of WES. COL Dwayne G. Lee, CE, is the present Commander and Director. Dr. Robert W. Whalin is Technical Director. The Head Director of MT-TNO was I. C. J. Duyverman, and Under Director at Delft was Dr. W. H. J. M. Wientjes.

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PRELIMINARY ASSESSMENT OF BIOACCUMULATION OF METALS AND ORGANIC CONTAMINANTS  
AT THE TIMES BEACH CONFINED DISPOSAL SITE, BUFFALO, NEW YORK

PART I: INTRODUCTION

Times Beach Confining Disposal Site

1. The Times Beach confined disposal site was constructed in 1971 along the shore of Lake Erie near the mouth of the Buffalo River at Buffalo, N. Y. (Figure 1). The site, 46 acres (0.19 km<sup>2</sup>) enclosed by a dike, received  $7.2 \times 10^5$  m<sup>3</sup> of dredged material from the Buffalo Harbor from 1972 to 1976. The sediments apparently were contaminated by the industries along the waterfront, including an oil refinery, two steel plants, an aniline dye chemical plant, and milling facilities.

2. The disposal site was only partly filled. The surface of the dredged material layer (about 3 to 4 m deep) sloped from above ground-water level at the mouth of the former disposal pipe to below the water level of Lake Erie. This resulted in aquatic, wetland, and upland disposal environments. When disposal activities were interrupted, plants and animals rapidly began to colonize these environments, and a prolific wildlife community evolved. Local ornithologists requested that further disposal activities at Times Beach not be implemented in order to preserve the very rich bird fauna. From the aerial photograph (Figure 2), it can be seen that about 50 percent of the area is still open water, 25 percent is a wetland, and the remaining 25 percent is an upland, wooded habitat.

3. Available information at the US Army Engineer Waterways Experiment Station (WES) showed the presence of potentially toxic metals and organic compounds in Times Beach disposal site materials. Previous plant bioassays\* on these materials did not show significant uptake of contaminants, and the

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\* B. L. Folsom, Jr. Unpublished. "Interpretive Summary, Evaluation of Availability and Plant Uptake of Contaminants from Dredged Material from Buffalo, New York; Toledo, Ohio; and Cleveland, Ohio," Memorandum for Record, 29 January 1982, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

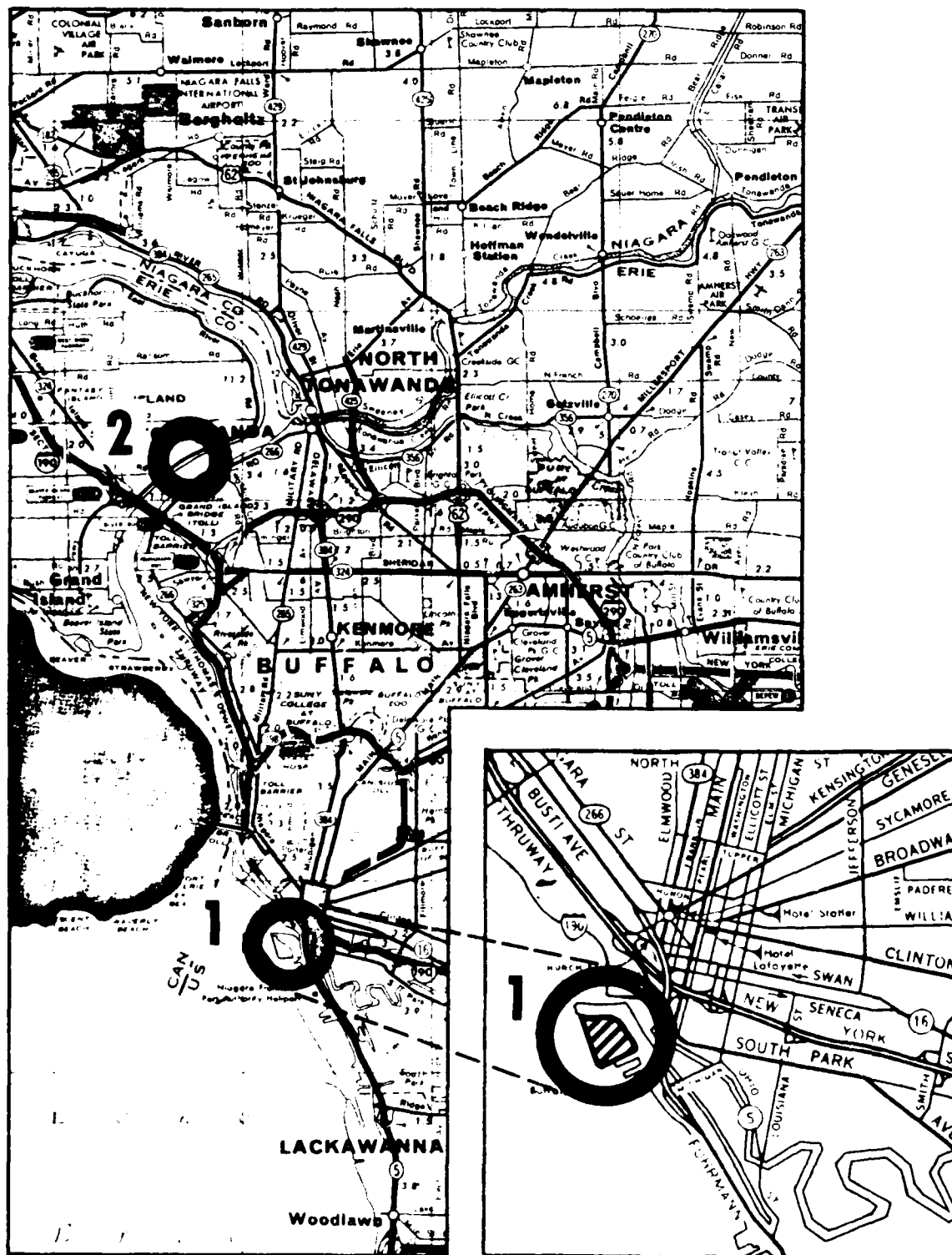


Figure 1. Positions of Times Beach confined disposal site (1) and the selected reference area (2)



4. Because habitats typical for all three disposal alternatives are present, this area offers the unique opportunity to compare contaminant mobility in relation to disposal strategy.

#### Reference Sites

5. To decide whether or not contaminants were accumulated in organisms as the result of their presence in the dredged material and not by secondary pollution from emissions deposited via the atmosphere, flooding, etc., the monitoring of nearby reference sites was essential. These sites were selected by the US Army Engineer District (USAED), Buffalo. The reference area for fish collections was the Buffalo River at the point where it flows into Lake Erie, just north of the disposal site. This site was selected because many species of fish-eating birds foraging at Times Beach were seen on that spot. The reference area for earthworm collection was between the East River Road and the East Niagara River, near the River Oaks Golf Course (Figure 1). Soil profiles were examined, and the vegetational types were identified. About 1 m of silt loam and fine sands were present above a compact grey glacial till. The top layer of 0.2 m proved to be humus rich. The area appeared to have been undisturbed physically by human activities.

#### Objectives

6. As a result of discussions between The Netherlands Organization for Applied Scientific Research (TNO), the WES, and the USAED, Buffalo, the following objectives were defined:

- a. To assess the potential uptake of contaminants from Times Beach upland and wetland dredged material by soil-inhabiting macroinvertebrates.
- b. To provide an inventory of contaminants in fishes and soil-dwelling macroinvertebrates living at the disposal site.

All of these studies were preliminary in nature and were designed to point out areas in which further research was needed. This document is the end product of a preliminary assessment and should not be construed as a final statement of conditions at the Times Beach confined disposal site.

## PART II: MATERIALS AND METHODS

### Rearing of Worms

7. Earthworms (*Eisenia foetida*) were obtained from a local bait dealer and were held at room temperature in worm beds at the WES in an artificial soil mixture consisting of peat moss and manure. The worms were fed with horse manure as needed.

### Terrestrial Animal Bioassay

8. A terrestrial invertebrate bioassay was used to assess contaminant uptake from dredged material by terrestrial invertebrates. The earthworm serves in this test as a model soil-inhabiting invertebrate. Earthworms were chosen because they ingest large quantities of silt materials, occupy the beginning levels of many terrestrial food chains, and are important in recycling nutrients in relation to plant life. *Eisenia foetida* was also chosen because of its recognized value and approved use in toxicity testing by the European Economic Community (EEC) and the Organization for Economic Cooperation and Development (OECD) (C. A. Edwards 1983) and the ease in rearing of laboratory stocks with controlled low contaminant concentrations.

9. This bioassay was applied simultaneously under standardized environmental chamber conditions (temperature, moisture, etc.) and under field conditions. Dredged material was collected at stations along transects at the Times Beach confined disposal site, extending from the waterfront (A1B1 in Figure 2) in the direction of the former disposal pipe (A8) and from the waterfront straight toward Furhmann Boulevard (B8). A 20-cm- (8-in.) diam soil auger was used to collect the surface mineral layer after all plant litter had been removed. The resulting soil core was 25 cm (10-in.) in depth and was partly mixed by the action of the auger. Two identical cores were taken side by side, one for laboratory use and the other for field studies. Experiments under standardized environmental chamber conditions were performed at the WES. For experiments under field conditions, worms were exposed at each station at Times Beach (A8, A1B1, and B8).

10. The bioassays were conducted in white polyethylene containers (ca. 0.20 by 0.3 m, diam by height) with perforated bottoms (five holes covered

with 1-mm mesh screening) and screened lids (Figure 3). Containers were filled with about 7 l of soil material and stocked at random with subsamples of about 150 worms ( $20 \pm 0.5$  g). The manure-amended rearing medium was used as a physical control for temperature and flooding/drying in both field and laboratory studies.

11. In the laboratory, the containers with soil material were placed in a water dish (Figure 3) with deionized water for 48 hr prior to the stocking of worms. The water level, a temperature of  $15^{\circ}$  C, and low light conditions were maintained in an environmental chamber throughout the exposure period. A water-saturated condition at the bottom and a relatively dry condition at the top allowed the worms to select optimum moisture conditions. No food was added during the study.

12. In the field, the containers were placed in the soil at each of the different transect stations with the soil surface inside the container at the same level as that outside. Otherwise, the field study was treated similarly to the laboratory study.

13. At the end of a 32-day exposure period, the worms were recovered by hand sorting, counted, washed in deionized water, and allowed to purge their gut contents for 48 hr at  $10^{\circ}$  C on moistened filter paper. The worms were washed again, and the filter paper was changed at 24 hr. After purging was completed, the worms were washed again, weighed in acid-cleaned glassware, killed by freezing, and stored at  $-20^{\circ}$  C.

### Field Collections

#### Native worms

14. Native worms were collected at the Times Beach confined disposal site and the reference area situated along the east side of the Niagara River. Samples of native worms were collected in August 1983 by digging and hand sorting and were identified according to species. Individuals of the same species were separated and pooled by sample prior to purging. After purging, the worms were frozen and transported to TNO for analysis.

#### Fish

15. Fish species were collected in August 1983 from the open water of the Times Beach confined disposal site and from a reference area in the Buffalo River predominantly by seining and to a lesser extent by hook and line.

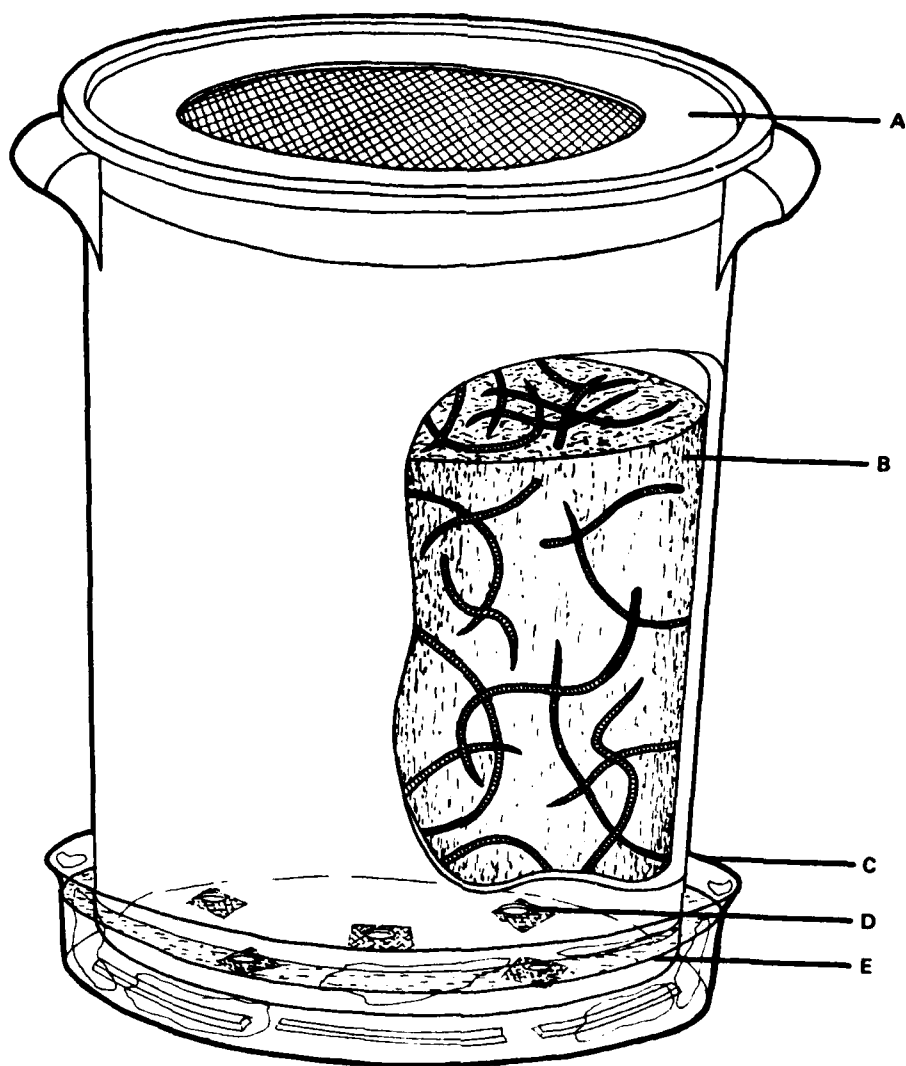


Figure 3. The WES earthworm bioassay container:  
 (A) screened top; (B) substrate; (C) water dish;  
 (D) screened holes, 1/4-in. diam; (E) water  
 level

Each species was pooled into one sample. In order to make a risk assessment for local human consumption, fillets of the lateral musculature were prepared. Liver tissues were prepared to evaluate the presence of contaminants on a physiological basis and to compare Times Beach with the reference site for contaminants that do not accumulate in muscle tissue (e.g., cadmium). Individuals of the same species were pooled, packed in polyethylene bags, and stored at  $-20^{\circ}\text{C}$ . Prior to dissection of livers and muscle tissue, all

specimens were measured (total length) and weighed. Livers and muscle tissues were pooled by species and stored at  $-20^{\circ}\text{C}$  in acid-washed glassware.

#### Plants

16. Four different plant species from the wetland area were designated by the USAED, Buffalo, as important food sources for local bird populations. Samples of these species were collected with the soil around their roots. Fresh and dry weights of plant tissues were measured, and samples were stored for later analysis. All plant samples were superficially washed with deionized water. Dead leaves, stems, and seeds were dried at  $60^{\circ}\text{C}$ . Green leaves were frozen in acid-washed glassware and stored at  $-20^{\circ}\text{C}$  for subsequent chemical analyses.

#### Analysis

17. It was decided to restrict the chemical analysis of contaminants to metals (cadmium (Cd), copper (Cu), mercury (Hg), and arsenic (As)), polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs), as specified in Table 1. Also, in the field earthworm experiment, a selection was made of about six samples of experimental worms to be analyzed, roughly covering the complete transect, and four samples of control worms.

18. Remaining amounts of the samples will stay properly stored in the TNO specimen bank for at least 3 years for possible future work.

19. Prior to analysis, all tissue samples were homogenized in the glassware in which they were to be stored. An Ultra Turrax<sup>®</sup> was used to homogenize the tissues. The Ultra Turrax<sup>®</sup> was modified by TNO and equipped with a solid titanium milling device. The homogenates were divided into subsamples for the various analytical procedures. Soils and sediments were thoroughly mixed prior to analysis.

#### Dry and ash weights

20. Subsamples of about 0.5 g each of wet homogenate were weighed to 0.0001 g, dried for 16 hr at  $105^{\circ}\text{C}$ , reweighed, ashed for 4 hr at  $600^{\circ}\text{C}$ , cooled in a desiccator to  $20^{\circ}\text{C}$ , and reweighed. Percentages of water and ash-free dry material were recorded and used to convert the concentrations of contaminants from a wet-weight to a dry-weight basis (soil materials) or an ash-free dry-weight basis (tissues). The percentage of ash-free dry material

Table 1  
Nomenclature of PCB and PAH Components Under Study  
with Reporting Code\* Numbers

			<u>PCB Components</u>
28	2,4,4'	-	trichlorobiphenyl
52	2,2',5,5'	-	tetrachlorobiphenyl
49	2,2',4,5'	-	tetrachlorobiphenyl
70	2,3',4,'5	-	tetrachlorobiphenyl
101	2,2',4,5,5'	-	pentachlorobiphenyl
87	2,2',3,4,5'	-	pentachlorobiphenyl
153	2,2',4,4',5,5'	-	hexachlorobiphenyl
138	2,2',3,4,4',5'	-	hexachlorobiphenyl
180	2,2',3,4,4',5,5'	-	heptachlorobiphenyl
			<u>PAH Components</u>
1	phenanthrene		12 perylene
2	anthracene		13 benzo(b)fluoranthene
3	fluoranthene		14 benzo(k)fluoranthene
4	pyrene		15 benzo(a)pyrene
5	3,6-dimethylphenanthrene		16 dibenzo(a,j)anthracene
6	triphenylene		17 dibenzo(a,i)pyrene
7	benzo(b)fluorene		18 benzo(g,h,i)perylene
8	benzo(a)anthracene		19 indeno(1,2,3-c,d)pyrene
9	chrysene		20 3-methylcholanthrene
10	benzo(e)pyrene		21 anthanthrene
11	benzo(j)fluoranthene		

\* PCB codes are those of the International Union of Pure and Applied Chemistry. The PAH codes are those used internally for convenience by TNO.

from the soil materials was used as an estimate of the percentage of soil organic matter.

#### Heavy metals

21. Concentrations of Cd, Cu, Hg, and As in earthworm and fish tissues were determined with destructive neutron activation analysis (NAA). Approximately 0.2 to 0.5 g of wet tissue was exposed to a neutron flux of  $10^{13}$  neutron·cm<sup>-2</sup>·s<sup>-1</sup>. After a wet destruction procedure and a separation on ion exchange resins,  $\gamma$  energies were measured: Cd at 336 KeV, Cu at 511 KeV, Hg at 77 KeV, and As at 559 KeV.

22. Two soil samples from Times Beach, one from the upper 0.3 m (at station B8) and one of unconsolidated material from an approximate depth of 1.0 to 1.2 m (at station A3), were first analyzed for a wide range of elements with instrumental neutron activation analysis (INAA). With this method, lead (Pb) cannot be assessed because it is not activated by neutrons. Some of the elements in these two samples were also analyzed by atomic absorption spectrometry (AAS). It should be noted that INAA also analyzes for elements in the crystalline matrix and, therefore, always yields somewhat higher concentrations than the AAS method. Concentrations of Cd, Cu, Hg, and As in all other soil samples were determined by AAS after element-specific wet destruction of about 2.5 g of material. Cd was measured by Electro Thermal (ET) AAS, Cu by Flame (F) AAS, Hg by Cold Vapor (CV) AAS, and As by Hydride Generation (HG) AAS.

#### Organochlorine contaminants

23. Concentrations of PCBs and hexachlorobenzene (HCB) were determined by gas chromatography (GC). Mirex proved to be absent and was used as an internal standard. Soil samples (~5 g, spiked with Mirex) were extracted, and the extracts were cleaned by chromatography over alumina and dried over sodium sulfate. Tissues (1 to 4 g) were treated in the same way, and proteins were enzymatically broken down.

24. After cleanup, the extracts were analyzed on a 50-m fused silica CP Sil 13B column with electron capture detection. Each series of eight samples was accompanied by a blank and three standard samples with different concentrations of HCB and PCB isomers. The PCB isomers determined were those selected by a Dutch standardization committee on PCB analysis on the basis of their general occurrence and analytical accessibility as indicators.

25. The sensitivity of the electron capture detector was monitored by including one "GC standard solution" sample, containing all substances to be determined for every five real samples, blanks, and/or standards. Peak identification was based on retention times, and peak height was used for quantification. Any work outside the linear range of the detector was avoided. The recovery percentage of the procedure followed here is in the order of 80 to 90 percent. The peak identification was confirmed for two samples by GC coupled to mass spectrometry (MS). The GC-MS analysis also revealed the presence of considerable amounts of aliphatic hydrocarbons, diphenylhydrazine, chloroanthraquinone, and aminobiphenyl.

#### PAHs

26. Concentrations of PAHs were determined by high performance liquid chromatography (HPLC). Soil samples (~5 g) were spiked with dibenzo(a,h)-anthracene, extracted, and taken up in methanol. Tissues (~2.5 g) were treated with sodium hydroxide, extracted, and then cleaned over alumina. After cleanup, the extracts were analyzed on a 250- by 4.6-mm reverse phase C18 column with a methanol-water gradient and fluorescence detection. A number of spiked, uncontaminated tissue samples were treated in the same way, as well as a number of blanks. The PAH components that were analyzed are a standard series that is routinely analyzed at TNO laboratories.

27. Peak identification was based on retention times and supported by fluorescence behavior of the components, and quantification was based on peak height. Because unusually high concentrations of benzo(a)pyrene (B(a)P) were detected in some tissue samples, two of these samples (worm tissues) were chromatographed under different conditions and with an excitation and emission wavelength combination that is highly specific for B(a)P. The B(a)P peaks were trapped, and a full fluorescence spectrum was made. This spectrum fully confirmed the identification of benzo(a)pyrene. The recovery rate of the procedures that were followed ranged from 80 to 120 percent for tissues and from 80 to 100 percent for soil materials.

#### Data recording procedure

28. All chromatographs are directly coupled to a CIS Lab Automation System, which, in turn, is coupled to a Hewlett Packard HP-1000 computer. All appropriate data are filed on tape and can be reproduced off-line. Experimental treatments were unreplicated because of budget constraints and the

preliminary nature of the study. Therefore, data were not subjected to a statistical analysis.

### PART III: RESULTS AND DISCUSSION

#### Times Beach Confined Disposal Site

29. The Times Beach confined disposal site has evolved into an apparently productive ecosystem during the last decade. Although the site is still in a successional stage of development, a high diversity was noted for both floral and faunal components.

30. Compared with the situation in 1981 when investigators from the WES first visited the site, the *Typha* sp. (Figure 2) has extended towards Fuhmann Boulevard, overgrowing a former, larger sedge meadow. It was also observed that the area of the former sedge meadow has become wetter. Borings at different places in the site revealed that materials from below the level of the ground-water table still had a semiliquid consistency (Figure 4). The

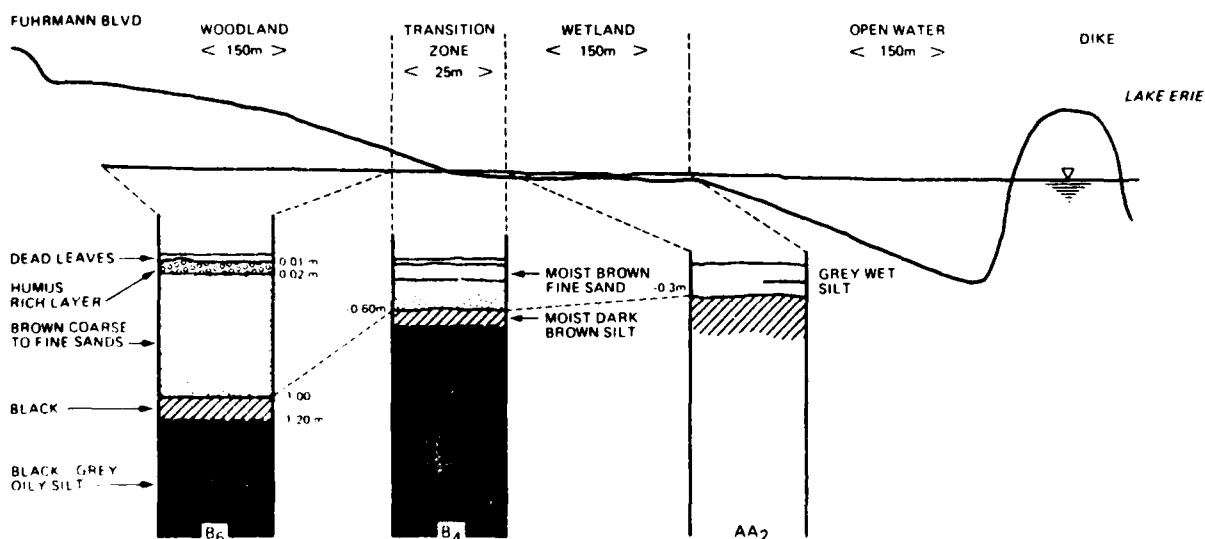


Figure 4. A transect through Times Beach confined disposal site diagramming the profiles in the cores

increased moisture may be caused by further consolidation of these materials and subsidence of the overlying layers or by higher lake levels.

31. The unconsolidated material had a greyish color, appeared highly reduced, and smelled rather oily. The surface material, especially in the woodland, had a quite "natural soil" appearance and odor. Except for a

reddish color, probably caused by iron-oxides, no visual suggestions of contamination were found in this layer.

32. The occurrence of the reduced material was clearly determined by the ground-water level. This reduced layer also contained the more highly contaminated material. There has been no capping with clean material, and the soil texture just above and just below the ground-water level seemed to be the same. It appeared that the level of contamination of the more oxidized dredged material had changed with time.

33. Three types of malformations (which have not been further investigated) were noticed in two plant species. In cattails (*Typha latifolia*), occasional crinkling of the leaves and malformations of flowering and seed production were observed. Furthermore, the growth of cottonwood trees (*Populus deltoides*) was clearly stunted, resulting in heavily cracked bark and thin trunks. It was not clear whether or not these phenomena were caused by the presence of certain contaminants.

#### Earthworm Experiments

34. The basic experimental data for the worm bioassays are summarized in Table 2. At the outset, each test group contained 20.0 to 20.2 g of worm biomass (nonpurged wet weight). From this table the following remarks can be made:

- a. Smaller worms were used for the laboratory study than for the field experiment.
- b. In both field and laboratory studies, some of the worms were lost for unknown reasons (mortality, escapes, etc.).
- c. In the field study, some samples were lost (100-percent mortality or escape) because of flooding during the experiment at the wettest stations.
- d. The percentage of water and ash-free dry tissues were rather constant for all tissue samples. Variations caused by rinsing and handling were excluded from the interpretation of the analytical data by expressing them on an ash-free dry-weight basis.
- e. A high variation in ash-free dry weight per worm was encountered in the field bioassay. This variation, as can be seen by comparing the controls of the field with those from the growth chamber experiments, is apparently caused by the extensive differences in moisture and temperature along the transect, interacting with worm activity. Because the manure

Table 2  
Basic Data for the Laboratory and Field Earthworm Experiments

Station	Field					Laboratory				
	# In*	# Out	Purged Wet Weight g	Water, %	Ash-Free Dry Worm mg	# In†	# Out	Purged Wet Weight g	Water, %	Ash-Free Dry Worm mg
R8	110	40	5.32	85.01	18.77	187	144	19.99	85.30	13.28
B7	104	9	0.54	82.81	9.78	194	155	20.19	85.36	13.28
R6	104	17	2.32	85.13	18.98	164	137	16.11	84.91	13.95
B5	116	21	3.40	84.08	22.76	180	102	11.12	84.29	14.02
B4	110	52	6.63	85.04	17.99	171	141	16.18	86.10	12.48
B3	113	25	3.16	--	--	172	142	15.53	86.21	12.34
B2**	118	0	--	--	--	153	142	16.18	86.30	12.49
A, B1**	115	0	--	--	--	185	166	12.39	82.77	14.98
A, B1**	112	0	--	--	--	--	--	--	--	--
A2	105	23	2.97	83.48	19.78	179	127	14.64	85.15	13.10
A3	111	28	4.31	84.62	21.01	194	131	20.05	88.31	10.66
A4	111	26	2.20	84.29	9.99	191	109	13.65	85.37	13.31
A5	114	42	4.89	84.48	16.79	160	112	14.52	86.16	12.80
A6	115	36	4.30	84.17	16.88	165	148	16.73	85.46	13.15
A7	112	19	2.66	84.84	10.36	207	159	17.75	85.10	13.45
A8	111	51	8.76	85.04	23.00	182	133	18.17	86.12	12.98
R8	112	98	18.12	85.62	25.00	--	--	--	--	--
R6	108	0†	--	--	--	--	--	--	--	--
B4	102	66	12.70	85.41	26.46	--	--	--	--	--
R2	107	73	19.72	85.39	37.09	--	--	--	--	--
A1 B1**	114	10	3.67	86.22	46.98	--	--	--	--	--
A3	109	71	13.51	82.99	30.45	--	--	--	--	--
A5	117	84	15.43	85.19	25.72	--	--	--	--	--
A7	110	88	16.15	85.89	24.43	--	--	--	--	--

(Continued)

\* Approximately 20-g fresh weight.  
 \*\* Subjected to unexpected flooding.  
 † Died during transit.

Table 2 (Concluded)

Station	Field				Laboratory			
	# In*	# Out	Purged Wet Weight g	Ash-Free Dry Water, %	Ash-Free Dry Z	Ash-Free Dry -1 Worm mg	Purged Wet Weight g	Ash-Free Dry Water, %
Manure 1	175	161	46.04	86.44	12.88	36.83	46.04	86.44
Manure 2	176	158	41.93	85.89	13.36	35.45	41.93	85.89
Manure 3	170	148	46.30	87.97	11.51	36.01	46.30	87.97
Manure 4	188	177	49.20	86.98	12.30	34.19	49.20	86.98

controls in the growth chamber experiment yielded the largest weight increase with the smallest variation between controls (as was expected), it was concluded that the growth chamber experiment would assess maximum contaminant uptake in a reproducible way. It was further decided that all worm samples of this experiment were to be analyzed in order to determine maximum potential contaminant bioaccumulation along the transects. From the worm samples of the field experiment, a selection was made for analysis for comparison with the laboratory bioassay.

- f. Potential for growth of *Eisenia foetida* in Times Beach dredged material is shown in Figure 5 in relation to some soil variables. Clearly, the potential for growth on materials from the wetland is very limited.

### Field Collections

#### Native worm samples

35. Basic data concerning native worms collected at Times Beach (one species) and at the Buffalo reference site (three species) are given in Table 3. It was decided to analyze the two samples from the Times Beach confined disposal site (*Lumbricus rubellus*) and all three species of two plots (C and D) of the reference site (*L. rubellus*, *Octolasion lacteum*, and *Allolobophora chlorotica*).

#### Fish samples

36. Table 4 summarizes the species and numbers of fish that were obtained at Times Beach and the adjacent mouth of the Buffalo River. Yellow perch and pumpkinseed were analyzed because both species were available at the two sites. Rock bass and carp from Times Beach were also analyzed because of their recognized value for human consumption.

#### Plant samples

37. Table 5 summarizes the amounts of plant tissues that were collected at Times Beach from four individual specimens of four species. It was decided to store the plant samples for later analysis.

### Contaminants

38. To facilitate an overview of the Times Beach confined disposal site faunal habitat as a whole (Figure 6), this section of the report will be divided into three parts dealing with heavy metals, PCBs and HCB, and PAHs.

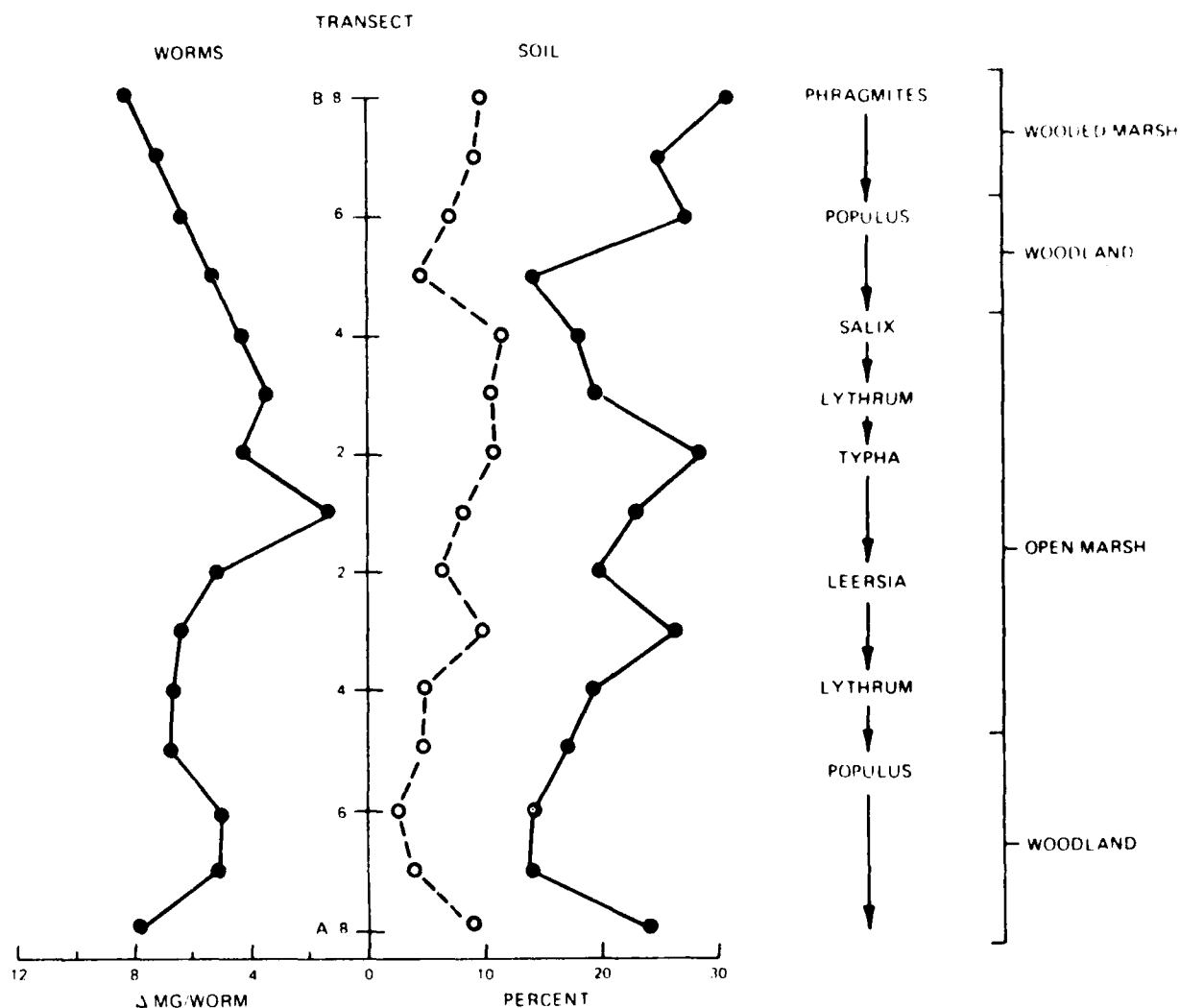


Figure 5. Transects at Times Beach (B8 → A8, top to bottom). Increase in weight of exposed worms (● = mg/worm ash-free dry tissue), composition of soil (o = organic matter as percent of dry weight; ● = percent of water), dominant species in vegetation, and habitat

Concentrations in tissues are reported on an ash-free dry-weight basis, and concentrations in dredged material on a dry-weight basis.

#### Heavy metals

39. The results of the INAA analyses (Table 6) show that besides Cd, Cu, Hg, and As, which were selected for analysis in all samples, other elements also occurred in elevated concentrations. Among these were zinc (Zn), lead (Pb), and chromium (Cr), which also were found previously by the WFS, as well as scandium (Sc), titanium (Ti), vanadium (V), manganese (Mn), iron (Fe), bromine (Br), molybdenum (Mo), antimony (Sb), and lanthanum (La). Some of

Table 3  
Native Worms Collected at Times Beach and  
the Buffalo Reference Area

<u>Location/Species</u>	<u>Plot</u>	<u>Number of Worms</u>	<u>Wet Weight, g</u>	<u>Water, %</u>	<u>Ash-Free Dry Wt., %</u>
Times Beach					
<i>Lumbricus rubellus</i>	A	85	33.17	83.52	12.78
	B	57	24.77	84.05	12.81
Buffalo Reference Area					
<i>Lumbricus rubellus</i>	A	21	5.24	85.59	12.59
	B	16	6.97	86.15	12.26
	C	29	14.42	85.36	12.63
	D	31	11.62	86.40	11.84
	E	19	7.98	86.64	11.09
<i>Oetolasion lacteum</i>	A	52	16.23	83.91	14.75
	B	44	15.04	84.10	14.18
	C	34	11.22	84.12	14.83
	D	25	8.58	--*	--
	E	76	19.08	84.72	13.82
<i>Alloleborphora chlorotica</i>	A	16	2.76	83.28	15.48
	B	32	6.35	83.69	15.18
	C	35	6.65	83.30	15.59
	D	22	4.49	--	--
	E	59	11.53	84.90	14.20

\* -- = Not analyzed.

Table 4  
Species and Number of Fish Caught at Times Beach  
and the Buffalo River

<u>Times Beach Species</u>	<u>Number</u>	<u>Buffalo River Species</u>	<u>Number</u>
<i>Ambloplites rupestris</i> (Rock bass)	13	<i>Moxostoma macrolepidotum</i> (Northern rednose)	1
<i>Ambloplites rupestris</i> (Rock bass, juv)	49	<i>Morone americana</i> (White perch)	1
<i>Cyprinus carpio</i> (Carp)	6	<i>Notomigonus crysoleucus</i> (Golden shiner)	3
<i>Lepomis gibbosus</i> (Pumpkinseed)	19	<i>Lepomis gibbosus</i> (Pumpkinseed)	6
<i>Perca flavescens</i> (Yellow perch)	2	<i>Perca flavescens</i> (Yellow perch)	6

Table 5  
Plant Material Collected at Times Beach, Weight in g·m<sup>2</sup>

Species	Replicate	Green Leaves	Green Stems		Seeds		Dead Leaves	
		Fresh	Fresh	Dry	Fresh	Dry	Fresh	Dry
<i>Carex stipata</i> (sedge)	1	79.48	111.47	26.07	59.32	24.35	8.59	2.55
	2	66.74	79.28	18.44	69.57	21.32	4.85	1.75
	3	94.10	97.69	23.91	106.26	38.87	2.78	1.70
	4	84.23	42.60	10.39	20.45	7.62	5.34	2.32
<i>Phragmites australis</i> (common reed)	1	55.02	185.25	40.66	--*	--	1.09	0.42
	2	60.18	135.39	32.06	--	--	2.12	0.90
	3	86.44	164.16	44.68	--	--	1.37	0.45
	4	38.35	109.44	25.99	--	--	1.14	0.35
<i>Scirpus atrovirens</i> (bulrush)	1	106.60	121.44	38.56	26.19	8.44	11.31	3.61
	2	150.45	352.84	77.92	84.85	19.88	3.41	1.49
	3	54.99	91.90	21.94	41.92	11.38	1.98	0.52
	4	126.18	254.37	64.59	98.81	27.71	2.55	0.62
<i>Typha latifolia</i> (cattail)	1	73.46	188.85	32.17	54.62	8.48	--	--
	2	107.12	174.95	28.35	32.43	4.98	5.44	1.76
	3	46.60	143.76	27.51	19.33	4.81	0.79	0.43
	4	154.14	352.94	42.45	65.36	8.45	14.77	2.33

\* -- = not analyzed.

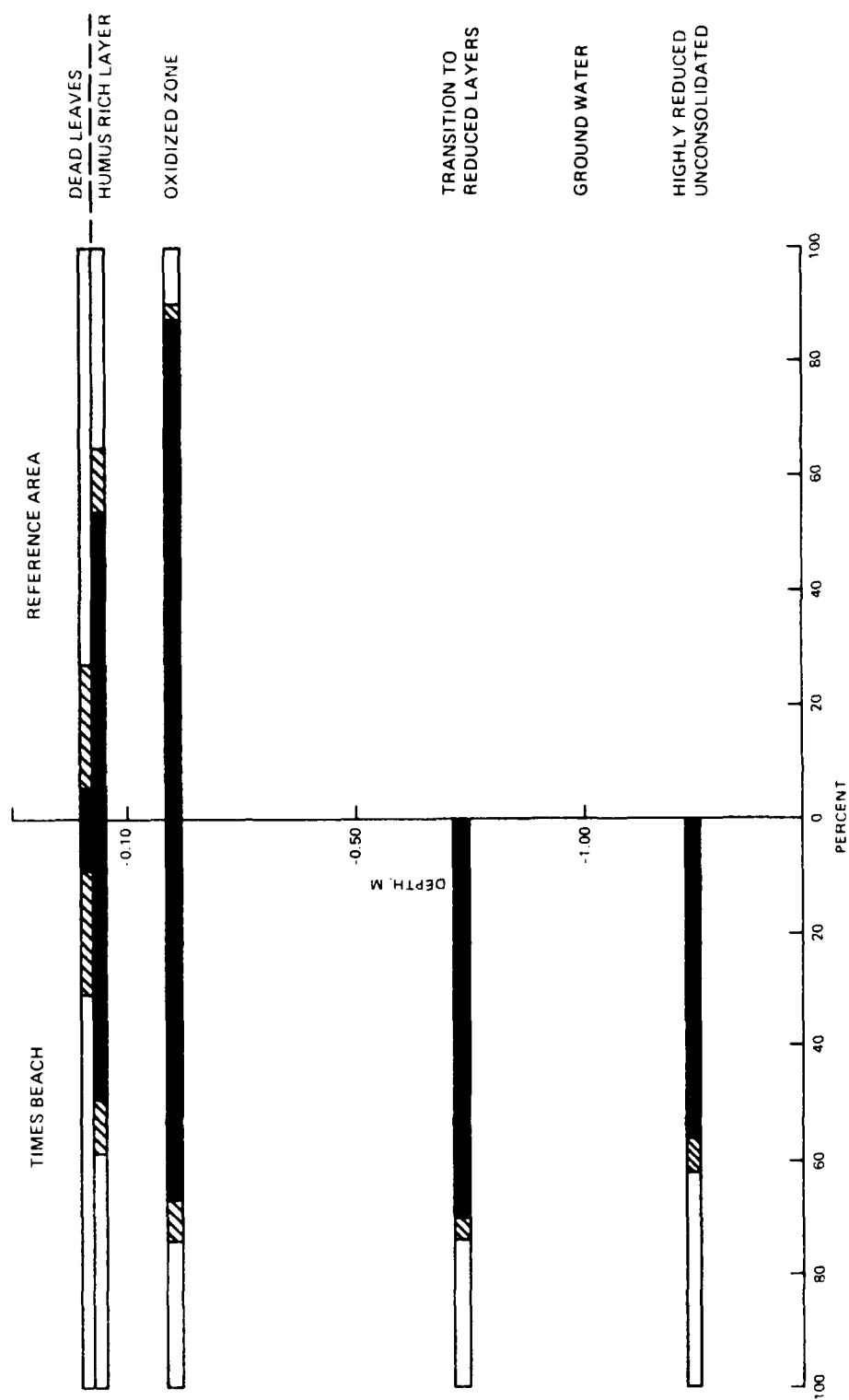


Figure 6. Profile analysis of upland soil cores from Times Beach (vicinity of Stations R5 and B6) and a reference area. Mean composition of soils in percent of water  $\square$ , organics  $\text{▨}$ , and solids  $\blacksquare$  at different depths

Table 6

Metal Concentrations in Dredged Material at Times Beach,  $\mu\text{g.g}^{-1}$  Dry Weight.

Two Samples Were Analyzed with INAA: Unconsolidated Material (A3-D)  
and Surface Woodland Soil (B8)

Element	INAA		AAS	
	A3-D*	B8	A3-D*	B8
Na	4,960.0	5,990.0		
Mg	10,200.0	15,600.0		
Al	53,000.0	85,000.0		
Cl	740.0	150.0		
K	15,100.0	20,400.0		
Ca	<30,000.0	<30,000.0		
Sc	10.00	10.32		
Ti	3,500.0	5,600.0		
V	80.0	126.0		
Cr	1,780.0	381.0		
Mn	820.0	1,325.0		
Fe	93,900.0	70,500.0		
Co	19.6	17.4		
Ni	<800.0	<900.0		
Cu	660.0	530.0	611.0	269.0
Zn	1,010.0	1,190.0		
As	193.0	61.8	159.0	53.0
Se	5.0	<7.0		
Br	70.4	22.4		
Mo	22.0	<20.0		
Cd	<30.0	<30.0	6.9	7.7
Sb	106.9	39.4		
I	<8.0	<20.0		
Cs	4.10	5.1		
Ba	360.0	400.0		
La	32.0	33.7		
Ce	50.0	<60.0		
Tb	0.85	0.95		
Hf	5.6	7.2		
Ta	2.2	1.18		
W	3.9	<7		
Au	<0.02	<0.02		
Hg	22.5	<5.0	14.9	7.5
Th	7.6	8.6		
U	2.8	3.8		
Pb	--	--	611.0	632.0

\* A3-D indicates materials from the deep, unconsolidated layer beneath the surface at transect point A3.

these last elements are frequently used as catalysts in organic chemical manufacturing processes.

40. With respect to soil depth, it can be seen that the concentrations of chlorine (Cl), Cr, Fe, Sb, Br, As, and Hg at the station studied are much lower in the top mineral layer than in the unconsolidated material underneath, probably as a result of leaching and volatilization from the upper mineral layer. The woodland top soil was enriched with magnesium (Mg), potassium (K), Ti, V, Mn, barium (Ba), and Cd in comparison with the underlying layers. These phenomena are illustrated for Cd and Hg in Figures 7 and 8. This apparent enrichment of the forest floor may be the result of uptake of metals by the trees, translocation of the metals to the leaves, and surface deposition of metals through successive yearly leaf fall.

41. The concentrations of Cd, Cu, Hg, and As in the mineral layer of dredged material along the transects at Times Beach are shown in Table 7, and Table 8 gives the concentrations of these elements in the experimental worms exposed to samples of that material in the environmental chamber. These results are graphically depicted for Cd and Hg in Figure 9. In general, it can be seen that the metal concentrations in the upper 0.3 m of material, which were collected with the exclusion of possibly formed humus, are higher in the wetland, where leaching and volatilization are restricted by the high ground-water level, than in the woodland parts of the transects. Metal uptake by the worms (bioavailability) appeared to be reduced in the wetland area compared with that in the woodland. The concentrations of Cu in worms tend to follow those in soil more closely (Figure 10).

42. A comparison of these worm data with the concentrations of heavy metals in native worms from Times Beach (Table 9) shows that the concentrations of Cu, Hg, and As are of the same order of magnitude in both experimental and field-collected (native) worms. For Cd, however, the concentrations in native worms are much higher than those in the experimental worms. This might be due to differences in species and/or slow uptake rates not reaching equilibrium concentrations during the 32-day experiment. Another reason might be that the native worms are exposed to the top layer, rich in humus, where they naturally occur, whereas the experimental worms were exposed only to the mineral topsoil with lower concentrations of Cd, as shown previously.

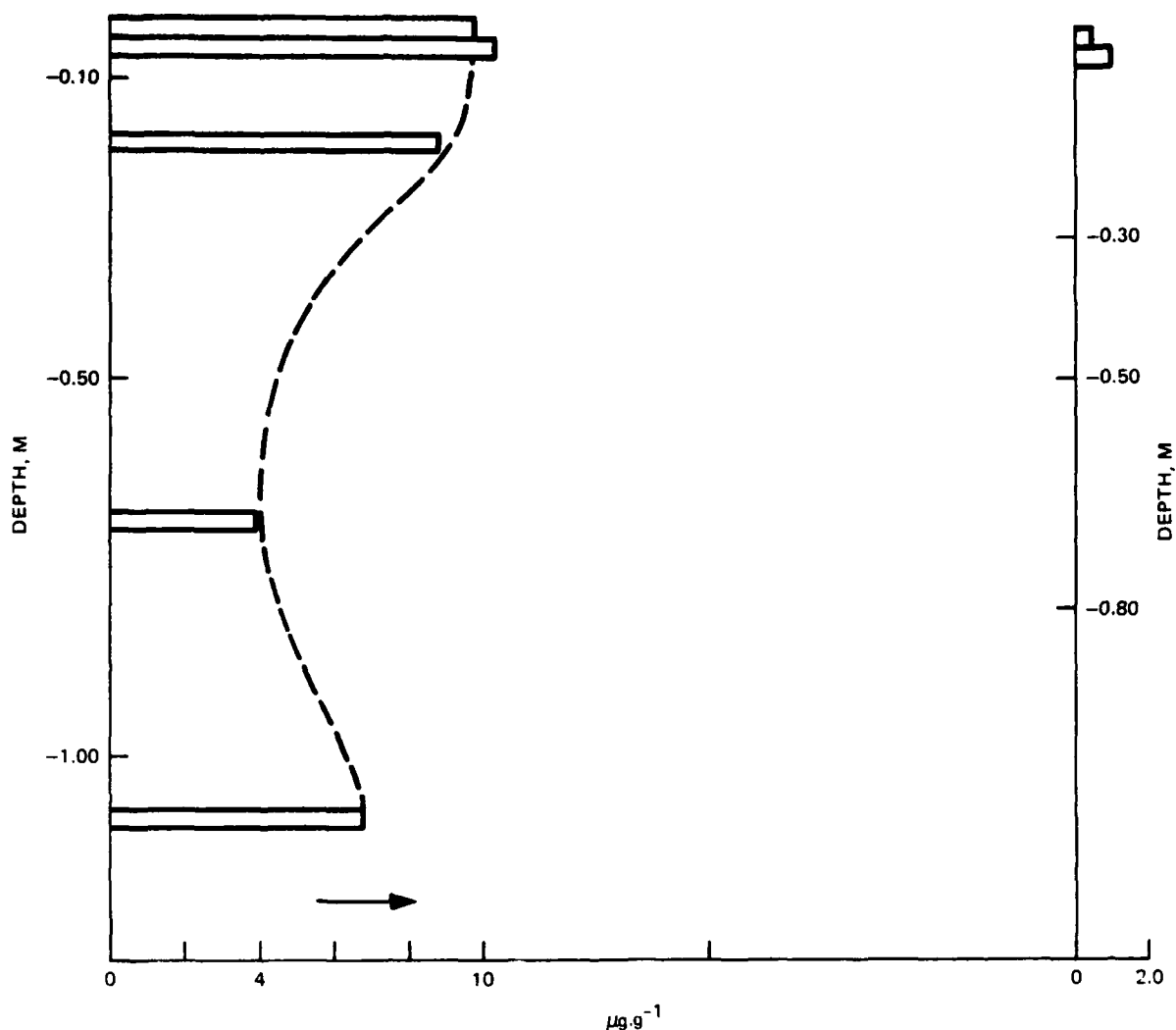


Figure 7. Vertical distribution of Cd in a woodland soil core from the vicinity of Stations B5 and B6 at Times Beach (left) and a reference area (right). Cd concentrations were less than detection limits at depths below -0.10 m in the soil from the reference area

43. Concentrations of metals in native worms from Times Beach generally appeared to be about 2 to 5 times as high as those from the reference site (Table 9). It should be emphasized that metal concentrations in worms from the reference site are somewhat elevated when compared with values cited in the literature for uncontaminated sites (Helmke et al. 1979, Carter 1983, Ma et al. 1983).

44. Concentrations of heavy metals in fishes from Times Beach and from a reference site (mouth of the Buffalo River) are given in Tables 10 and 11. These results indicate that Hg in yellow perch was more elevated at Times

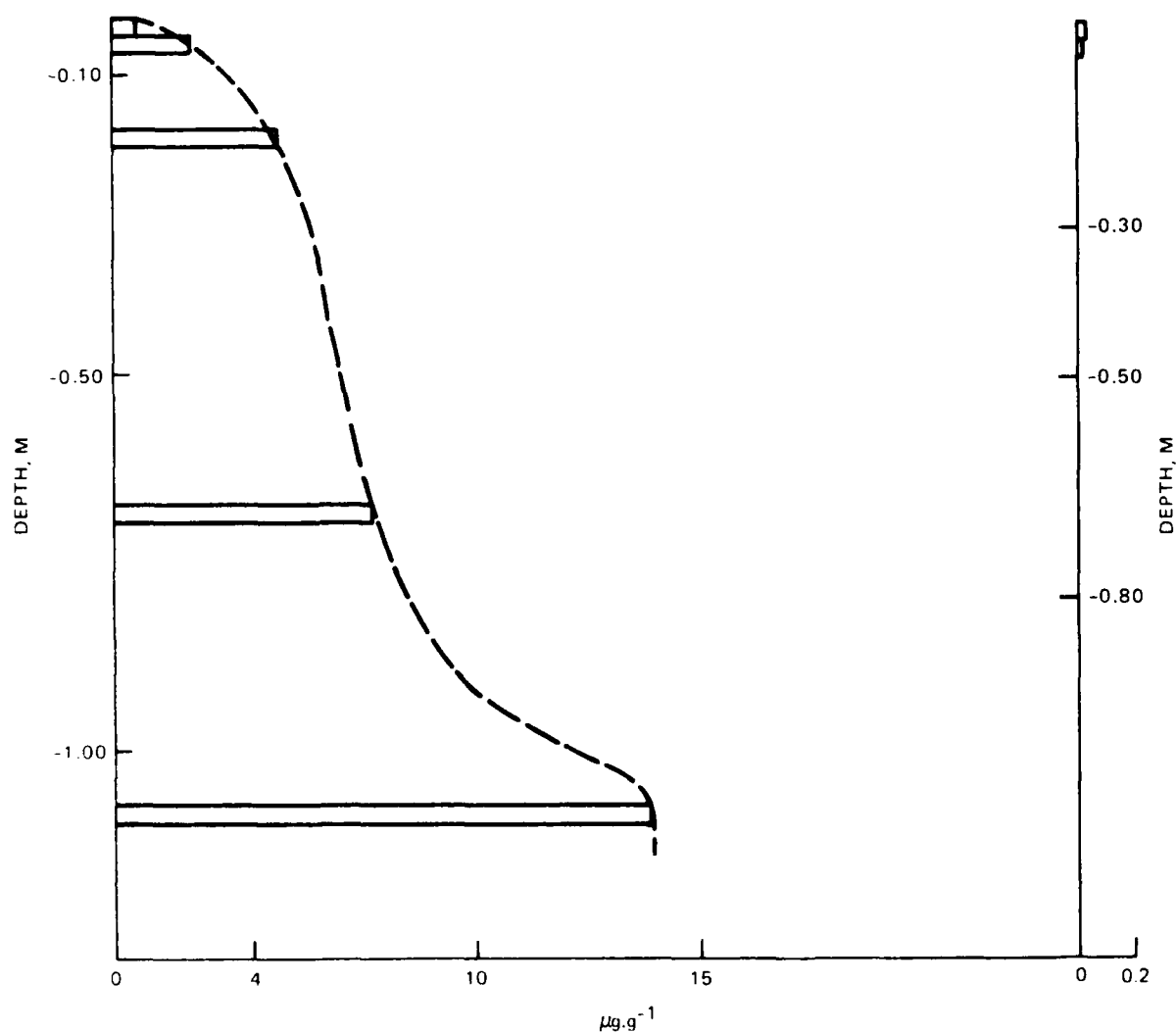


Figure 8. Vertical distribution of Hg in a woodland soil core from the vicinity of Stations B5 and B6 at Times Beach (left) and a reference area (right). Hg concentrations were less than detection limits at depth below -0.10 m in the soil from the reference area

Beach and approached the  $1\text{-}\mu\text{g}\cdot\text{g}^{-1}$  Food and Drug Administration (FDA) limit for edible fish tissues. The concentrations of metals in rock bass and pumpkinseed were higher, whereas those in carp and yellow perch generally were lower than the maximum metal concentrations in whole fish reported in the National Contaminant Biomonitoring program (Lowe et al. 1985). The results of the present study further suggest a potential Cd problem in the Buffalo River fish.

Table 7  
Metal Concentrations ( $\mu\text{g.g}^{-1}$  Dry Weight) in Times Beach  
Surface Dredged Material and a Control (Manure) Used  
in the Laboratory Study

<u>Station</u>	<u>Cd</u>	<u>Cu</u>	<u>Hg</u>	<u>As</u>
A8	2.10	116.0	2.10	25.0
A7	1.79	85.9	1.62	15.3
A6	0.76	60.0	1.52	20.0
A5	1.52	69.1	1.42	19.3
A4*	1.87	94.2	1.55	24.1
A3*	6.00	223.0	4.14	43.0
A2*	2.73	148.0	4.22	38.5
AlB1*	7.22	238.0	4.50	37.7
B2*	9.61	334.0	8.50	72.4
B3*	10.8	288.0	5.42	53.4
B4	10.4	308.0	5.18	47.8
B5	2.01	88.5	1.18	12.1
B6	5.33	228.0	4.78	58.8
B7*	6.63	224.0	3.94	36.4
B8*	7.74	269.0	7.45	53.0
Manure 1	0.39	16.5	<0.74	3.40
Manure 2	0.32	21.0	0.069	2.1

---

\* Wetland stations.

Table 8  
Metal Concentrations ( $\mu\text{g.g}^{-1}$  Ash-Free Dry Weight) in Experimental  
Worms Exposed to Times Beach Dredged Material in the Laboratory

<u>Station</u>	<u>Cd</u>	<u>Cu</u>	<u>Hg</u>	<u>As</u>
A8	8.86	27.7	0.482	21.1
A7	11.8	-	1.64	25.2
A6	6.54	17.3	0.981	17.5
A5	9.30	19.1	0.63	14.9
A4*	13.3	20.8	0.75	17.2
A3*	15.0	33.6	1.13	23.3
A2*	11.7	32.1	1.39	24.0
AlBl*	9.01	44.8	0.80	32.2
B2*	10.8	57.6	0.805	23.9
B3*	11.4	56.2	1.22	24.6
B4	12.3	52.7	1.04	15.9
B5	7.99	28.3	1.28	10.4
B6	17.6	36.2	1.14	35.3
B7*	16.0	35.2	1.13	33.0
B8*	16.0	46.7	1.77	53.8
Manure	3.04	10.1	0.059	8.72

---

\* Wetland stations.

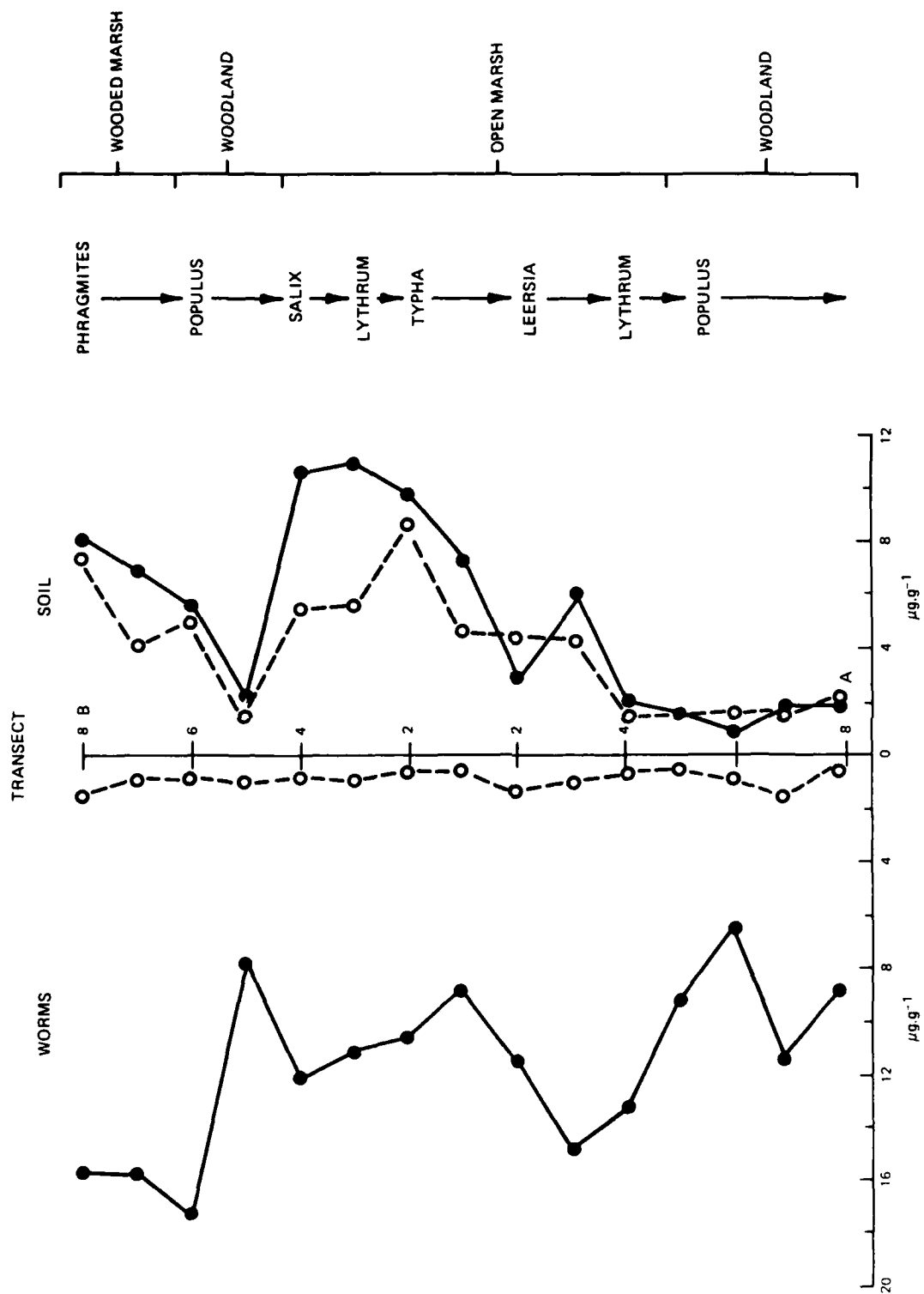


Figure 9. Hg (o) and Cd (●) concentrations in soil and worms exposed in the laboratory to soils from the transect B8 → A8

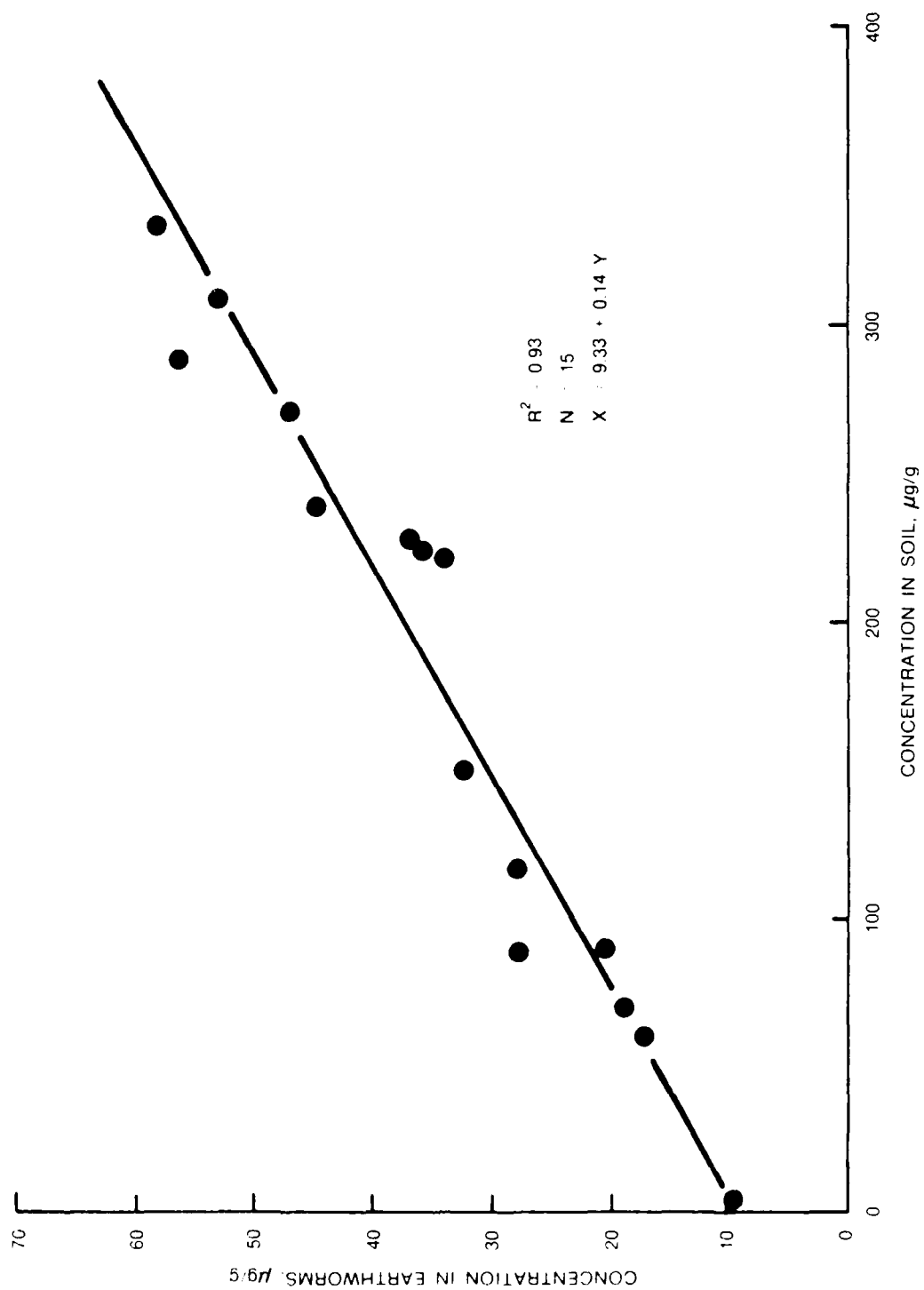


Figure 10. Relationship between Cu concentrations in the soil and in earthworms (*Eisenia foetida*) exposed in the laboratory

Table 9  
Metal Concentrations ( $\mu\text{g.g}^{-1}$  Ash-Free Dry Weight) in Native  
 Worms at Times Beach and a Reference Area\*

<u>Area</u>	<u>Species</u>	<u>Cd</u>	<u>Cu</u>	<u>Hg</u>	<u>As</u>
Times Beach	<i>Lumbricus rubellus</i>	113.0	59.7	1.33	30.8
		84.4	58.3	1.95	52.9
Reference	<i>Lumbricus rubellus</i>	17.6	20.2	0.469	8.84
		22.4	30.2	0.549	11.8
	<i>Allolobophora chlorotica</i>	24.3	11.4	1.76	10.8
		22.5	10.4	2.00	10.4
	<i>Octolasion lacteum</i>	36.5	12.5	1.77	6.47
		50.7	14.8	2.34	9.59

\* Data are the results of two analyses of each species.

#### PCB components and HCB

45. The concentrations of the different PCB components and of HCB in the soil materials are given in Table 12. The total of the PCB congeners analyzed in the soils/dredged materials at Times Beach was within the range of PCBs reported in freshwater sediments and fell well below the maximum reported for various drainage basins in the United States (National Academy of Sciences 1979). In the present study, only 9 (about 4 percent) of the 209 possible PCB congeners were analyzed. Most data reported in the literature were expressed on the basis of some PCB mixture, primarily one or more Aroclors. The total of the nine congeners analyzed in this study represents about 18, 34, and 21 percent, respectively, of the total PCB content of Aroclors 1242, 1254, and 1260 (Capel et al. 1985). If a broad assumption is made that Aroclors in environmental samples may have similar distributions of their component congeners as in Aroclor standards, then the total of the nine congeners analyzed may represent only a fraction of the total PCBs present in the soils/dredged material, as well as in the tissues of test organisms. The

Table 10  
Metal Concentrations ( $\mu\text{g.g}^{-1}$  Ash-Free Dry Weight) in Fishes at  
 Times Beach and the Adjacent Mouth of the Buffalo River

<u>Area</u>	<u>Species</u>	<u>Organ</u>	<u>Cd</u>	<u>Cu</u>	<u>Hg</u>	<u>As</u>
Times Beach	yellow perch	muscle	<0.013	2.44	1.16	0.214
		liver	0.042	1.32	0.102	0.936
	pumpkinseed	muscle	<0.019	3.3	0.717	0.579
		liver	0.316	8.00	0.355	1.89
	rock bass	muscle	<0.04	1.07	2.80	0.541
		liver	1.29	12.8	1.25	1.83
	carp	muscle	<0.025	2.73	0.767	0.801
		liver	0.125	8.37	0.252	0.751
Buffalo River	yellow perch	muscle	<0.020	1.92	0.428	0.161
		liver	0.280	3.96	0.053	0.575
	pumpkinseed	muscle	<0.028	1.99	0.730	0.534
		liver	1.26	10.9	0.363	1.82

Table 11  
Metal Concentrations ( $\mu\text{g.kg}^{-1}$  Fresh Weight) in Fishes at  
Times Beach and the Adjacent Mouth of the Buffalo River

<u>Area</u>	<u>Species</u>	<u>Organ</u>	<u>Cd</u>	<u>Cu</u>	<u>Hg</u>	<u>As</u>
Times Beach	veilow perch	muscle	<2.5	480	229.0	42.0
		liver	24.0	750	57.6	531.0
	pumpkinseed	muscle	<3.5	610	132.5	107.0
		liver	60.0	1,520	67.4	360.0
	rock bass	muscle	<7.0	220	563.0	108.5
		liver	230.0	2,300	221.5	327.0
	carp	muscle	<5.5	550	154.0	161.0
		liver	32.0	2,140	64.4	192.0
Buffalo River	yellow perch	muscle	<4.0	380	84.7	31.9
		liver	150.0	2,120	28.5	308.0
	pumpkinseed	muscle	<5.0	360	132.0	96.5
		liver	235.0	2,030	67.7	339.0

Table 12  
PCB Concentrations ( $\mu\text{g.kg}^{-1}$  Dry Weight) in Times Beach Surface Dredged  
Material and a Control (Manure)

Station	PCB Component*									HCB
	28	52	49	70	101	87	153	138	180	
A8	43	93	64	78	58	40	34	32	20.0	57
A7	33	110	76	120	44	27	15	20	7.7	95
A6	110	160	120	160	70	55	15	18	4.0	50
A5	140	180	140	220	60	39	17	37	7.1	94
A4**	94	230	170	220	89	59	26	40	12.0	160
A3**	84	290	190	230	130	89	48	79	21.0	320
A2**	130	220	160	210	110	76	42	41	15.0	110
A1B1**	54	180	110	150	71	48	23	51	7.7	130
B2**	55	220	150	120	140	100	71	71	34.0	110
B3**	64	340	220	290	190	120	79	110	37.0	330
B4	40	170	97	210	140	72	69	99	33.0	290
B5	15	36	22	47	26	13	21	28	12.0	190
B6	50	170	110	120	110	70	46	45	22.0	130
B7**	35	140	87	150	95	49	53	76	28.0	510
B8**	22	93	55	42	83	50	53	52	30.0	79
Manure 1	10	15	14	16	17	15	12	13	16.0	13
Manure 2	4.8	-	4.9	4.4	3.1	-	9.6	2.3	6.5	6.3

\* Nomenclature of PCBs given in Table 1.

\*\* Wetland stations.

highest concentrations of organochlorine compounds were found in the wetland materials, as was true for the heavy metals. The experimental worms exposed to these materials showed a marked increase of PCB and HCB concentrations (Table 13) in their tissues. This was apparently more directly dependent upon the concentrations in the substrate than was found for the heavy metals. The PCB and HCB concentrations in the earthworms generally ranged from about 3 to 10 times the concentrations in the soil/dredged material. This is in agreement with some reports on PCBs in earthworms (Greichus and Dohman 1980, Diercxsens et al. 1985).

46. In order to visualize the gradient in concentrations in worms and in soil along the transect, two components, a tetrachlorobiphenyl and a pentachlorobiphenyl, were selected. The concentrations of these components in worms and in the materials to which they were exposed are shown in Figure 11.

47. It is obvious that laboratory exposure of earthworms to materials from the wetland leads to high concentrations of PCBs and HCB in the worms, often exceeding  $1 \mu\text{g}\cdot\text{g}^{-1}$  for HCB and some PCB congeners. Concentrations of PCBs in the experimental worms exposed to woodland mineral soils in the laboratory (Table 13) were comparable with those in the native worms that were collected in the woodland (Table 14). No detectable amounts of PCBs were found in native worms from the reference area.

48. PCB and HCB concentrations in fishes are shown in Tables 15 and 16. Generally higher concentrations of both PCBs and HCB were found in fishes collected at Times Beach than in fishes from the aquatic reference site. The highest PCB and HCB levels in muscle tissues were found in the carp. Carp also had the highest concentrations of HCB found in the livers of species at Times Beach. The total concentration of the nine PCB congeners that were analyzed exceeded  $1\text{-}\mu\text{g}\cdot\text{g}^{-1}$  fresh weight in muscle tissues. The concentrations in the livers were much higher for all species. On a wet-weight basis, the highest total PCB concentration exceeded  $8 \mu\text{g}\cdot\text{g}^{-1}$  in the livers of yellow perch. The concentrations of PCBs in all species analyzed from both the Buffalo River and Times Beach exceeded the maximum (whole fish) levels reported (as Aroclors) for those species in the National Pesticide Monitoring Program (NPMP) for 1980-1981 (Schmitt, Zajicek, and Ribick 1985). It should be reiterated that the nine congeners analyzed in the present study may represent only a fraction of the total PCB present. Also, Schmitt, Zajicek, and Ribick (1985) reported PCB concentrations in the whole fish, whereas in the present

Table 13  
PCB Concentrations ( $\mu\text{g}\cdot\text{kg}^{-1}$  Ash-Free Dry Weight) in Experimental  
Worms Exposed to Times Beach Dredged Material in the Laboratory

Station	PCB Component*									
	28	52	49	70	101	87	153	138	180	HCB
A8	230	800	460	600	680	310	420	330	120	190
A7	160	740	510	950	420	220	180	230	64	1,200
A6	530	1,000	760	990	520	310	140	130	<46	350
A5	270	590	440	830	290	140	120	150	42	560
A4**	200	680	480	860	360	180	130	210	43	890
A3**	190	1,400	910	1,600	800	430	300	400	81	2,000
A2**	400	1,000	690	830	630	360	280	230	100	510
A1B1**	240	1,000	660	1,200	590	340	280	360	81	890
B2**	260	1,700	1,100	870	1,100	680	470	430	150	620
B3**	190	1,500	970	1,900	960	520	390	540	120	2,100
B4	110	1,000	570	1,500	810	400	410	570	120	1,800
B5	37	220	120	500	240	98	200	240	78	920
B6	150	870	540	430	630	360	290	250	100	560
B7**	57	460	280	830	430	200	270	340	94	2,500
B8**	60	680	340	<45	730	350	420	350	150	460
Manure	<32	<48	<45	<51	<54	<48	<39	<42	<51	19

\* Nomenclature of PCBs given in Table 1.

\*\* Wetlands stations.

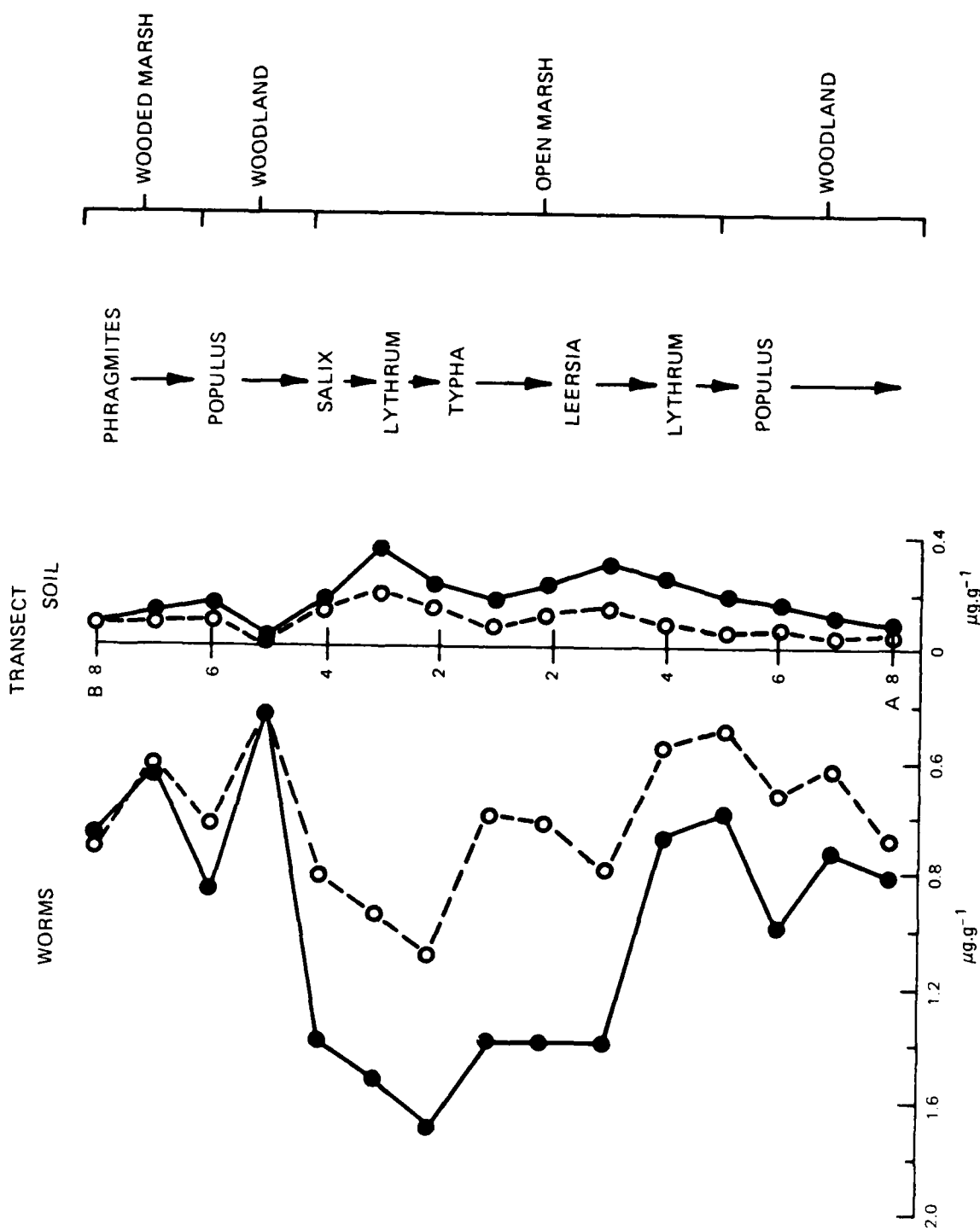


Figure 11. Concentrations of 2,5,2',5'-tetrachlorobiphenyl (●) and 2,4,5,2',5'-pentachlorobiphenyl (○) in soil and worms exposed to soils from the transect B8 → A8

Table 14  
PCB Concentrations ( $\mu\text{g} \cdot \text{kg}^{-1}$  Ash-Free Dry Weight) in Native Worms at  
 Times Beach and a Reference Area

Area	Species	PCB Component*									
		28	52	49	70	101	87	153	138	180	HCB
T.B.	<i>L. rub.</i> **†	126	460	220	330	320	160	130	130	50	260
		207	900	460	590	560	280	200	210	160	370
Ref.	<i>L. rub.</i>	all values below detection limits (<40)									
	<i>A. chl.</i>	all values below detection limits (<40)									
	<i>O. lac.</i>	all values below detection limits (<40)									

\* Nomenclature of PCBs given in Table 1.

\*\* Analyses of two samples.

† *L. rub.* = *Lumbricus rubellus*; *A. chl.* = *allolobophora chlorotica*; *O. lac.* = *Ocotolasion lacteum*.

study, the concentrations were reported in livers and lateral musculature. Consequently, the direct comparison of these data with reports in the literature may be highly misleading. The FDA tolerance limit for PCB ( $2 \cdot \mu\text{g} \cdot \text{g}^{-1}$  wet weight) is based presently upon total PCB in edible tissues. Therefore, a potential problem may exist with respect to the use of those fishes for human consumption.

#### PAH components

49. PAH components form a very diverse group of contaminants. In general, this group consists of unsaturated, aromatic, sometimes alkylated rings ranging from two to eight. PAH components differ greatly from each other in physical constants, toxicity, and carcinogenicity. Contamination with PAHs often results from combustion or other processing of fossil fuels, results from combustion or other processing of fossil fuels, as some of the components occur naturally in plants or are formed through the burning of wood (N. T. Edwards 1983, Blumer 1976, Andelman and Suess 1980).

Table 15  
PCB Concentrations ( $\mu\text{g.kg}^{-1}$  Ash-Free Dry Weight) in Fishes at  
Times Beach and the Adjacent Mouth of the Buffalo River

Area	Species**	Organ†	PCB Components*									
			28	52	49	70	101	87	153	138	180	HCB
T.B.	Y.P.	m	100	180	130	160	130	59	68	56	22	38.0
		l	1,800	3,400	2,500	2,900	2,300	840	750	580	330	580.0
	P.S.	m	150	290	210	290	210	110	120	100	50	46.0
		l	420	750	590	780	600	360	370	330	190	100.0
	R.B.	m	160	370	280	400	310	150	190	210	83	35.0
		l	200	5,200	4,000	5,800	5,200	2,500	3,300	3,700	1,500	360.0
	C.	m	630	1,100	830	1,400	570	280	260	310	110	190.0
		l	2,100	3,200	2,500	4,100	1,800	920	800	870	220	600.0
B.R.	Y.P.	m	26	38	26	27	41	23	63	50	33	4.4
		l	530	900	650	600	920	87	900	580	230	110.0
	P.S.	m	18	26	25	28	33	26	47	34	28	6.5
		l	42	70	50	64	90	25	130	93	73	15.0

\* Nomenclature of PCBs given in Table 1.

\*\* Y.P. = yellow perch; P.S. = pumpkinseed; R.B. = rock bass; C. = carp.

† m = muscle; l = liver.

Table 16

PCB Concentrations ( $\mu\text{g.kg}^{-1}$  Fresh Weight) in Fishes at Times Beach and  
the Adjacent Mouth of the Buffalo River

Area	Species†	Organ††	PCB Components*									$\Sigma^{**}$	
			28	52	49	70	101	87	153	138	180	PCB	HCB
T.B.	Y.P.	m	20.0	35.0	26.0	31.0	26.0	12.0	13.0	11.0	<4.3	175	7.5
		l	1,000.0	1,900.0	1,400.0	1,600.0	1,300.0	480.0	430.0	330.0	190.0	8,600	329.0
P.S.	m	m	28.0	54.0	39.0	54.0	39.0	20.0	22.0	18.0	9.2	280	8.5
		l	80.0	140.0	110.0	150.0	110.0	70.0	70.0	63.0	36.0	830	19.0
R.B.	m	m	32.0	75.0	56.0	80.0	63.0	30.0	38.0	43.0	17.0	430	7.0
		l	350.0	920.0	720.0	1,000.0	930.0	450.0	600.0	660.0	270.0	5,900	64.0
C.	m	m	130.0	220.0	170.0	270.0	120.0	56.0	53.0	62.0	22.0	1,100	38.0
		l	530.0	810.0	630.0	1,100.0	460.0	240.0	200.0	220.0	55.0	4,200	153.0
B.R.	Y.P.	m	5.1	7.5	5.1	5.3	8.1	<4.6	12.5	9.9	6.5	63	0.87
		l	280.0	480.0	350.0	320.0	490.0	47.0	480.0	310.0	120.0	2,900	59.0
P.S.	m	m	<3.3	<4.7	<4.5	<5.1	6.0	<4.7	8.5	6.1	<5.1	<48	1.2
		l	7.8	13.0	9.3	12.0	17.0	<4.7	24.0	17.0	14.0	115	2.8

\* Nomenclature of PCBs given in Table 1.

\*\* Total of the nine congeners analyzed.

† Y.P. = yellow perch; P.S. = pumpkinseed; R.B. = rock bass; C. = carp.

†† m = muscle; l = liver.

50. Because they always occur in a mixture (Neff 1979), only limited information is available on the individual components in relation to environmental effects, with the exception of benzo(a)pyrene (BaP), which has served as a model compound in many laboratory experiments dealing with mutagenicity, whereas naphthalene and phenanthrene, have been used for aquatic bioassay studies. Only limited information is available for the other individual components in relation to mutagenicity and toxicity (Verschuere 1983).

51. Differences in the physical constants are thought to have led to the component-specific behavior as illustrated for four components in Figure 12. Both the concentrations of anthracene and pyrene (damp saturation values are  $1.87 \times 10^7$  and  $7.44 \times 10^4 \mu\text{g} \cdot 10^3 \text{ m}^3$  of air, respectively) are nearly absent in the top layer, probably as a result of volatilization and possibly microbial degradation. The concentrations of benzo(a)anthracene and benzo(a)pyrene (damp saturation values are  $1.33 \times 10^3$  and  $75 \mu\text{g} \cdot 10^3 \text{ m}^3$  of air, respectively) hardly changed with soil depth. These latter two components are of importance because of their mutagenic potential, whereas the former two do not show this potential.

52. Because at Times Beach a mixture of PAH components is found with a component-specific physical behavior in time-related weathering and because the components differ greatly in environmental significance to each other, relevant information will be lost in a summing up of the concentrations of the different components into a single total PAH value. Table 17 provides the concentrations of individual PAH components along the transects in the upper layer of disposed sediments at Times Beach. Obviously, the highest concentrations are found in the wettest section of the transect (A2, A1B1, and B2). Remarkably lower concentrations are found in one of the woodland sections (A4 to A7). It is not clear whether this is due to differences in the original dredged sediments (increasing particle sizes in the direction of the disposal pipe) or to secondary weathering processes. In general, the concentrations of known mutagens like benzo(a)pyrene, dibenzo(a,i)pyrene, benzo(b)fluoranthene, benzo(a)anthracene, and chrysene should be regarded as rather elevated in comparison with many sediments and soils, which usually have PAH concentrations well below  $1 \mu\text{g} \cdot \text{g}^{-1}$  (Mallet, Perdriau, and Perdriau 1963, Brown and Starnes 1978). Contaminated harbor sediments, however, frequently have concentrations of PAHs exceeding  $1 \mu\text{g} \cdot \text{g}^{-1}$ .

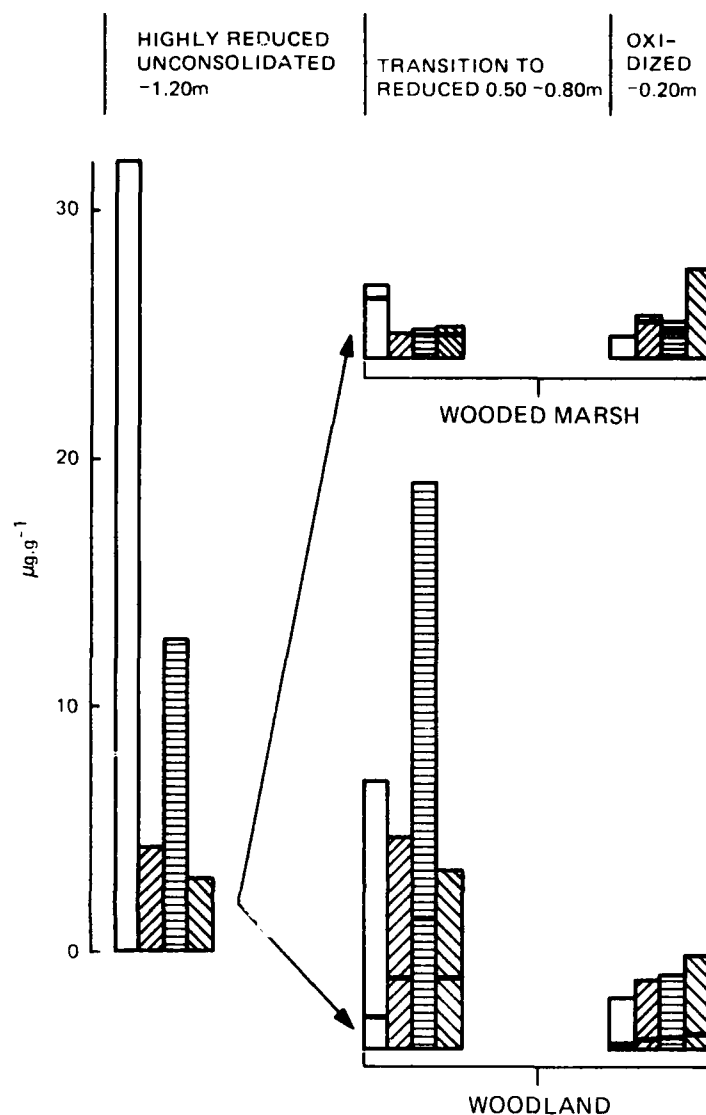


Figure 12. Concentrations of anthracene ( $\square$ ), benzo(a)anthracene ( $\text{▨}$ ), pyrene ( $\text{▩}$ ), and benzo(a)pyrene ( $\text{▧}$ ) in soil at different depths at Times Beach (Stations B8, B6, and A8A6)

53. The experimental worms that were exposed to these dredged materials showed various degrees of contaminant uptake (Table 18). Some of the components like benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and indeno(1,2,3,-c,d)pyrene reached the same concentrations in the worms as those in the dredged material to which they were exposed. The other components were generally concentrated to a lower extent.

Table 17  
PAH Concentrations ( $\mu\text{g}\cdot\text{g}^{-1}$  Dry Weight) in Times Beach Surface  
Dredged Material and Control (Manure)

Station	PAH Component*									
	1	2	3	4	5	6	7	8	9	10
A8	3.8	1.1	3.4	2.9	0.52	d†	0.58	2.8	3.0	1.8
A7	1.5	0.26	1.2	0.86	d	2.3	0.091	0.44	0.44	0.26
A6	0.54	0.18	0.59	0.53	0.068	d	0.075	0.37	0.33	0.32
A5	0.41	0.10	0.19	d	d	1.3	d	0.22	0.19	0.22
A4**	0.55	0.15	0.26	d	d	2.0	d	0.24	0.21	0.36
A3**	2.5	0.96	2.7	1.9	d	14.0	0.93	2.2	1.9	1.6
A2**	2.0	0.64	2.0	2.7	0.41	d	6.1	2.5	2.2	2.1
A1B1**	4.8	1.5	5.8	4.1	d	23.0	0.96	3.2	2.8	1.3
B2**	3.2	0.96	2.8	2.5	0.72	d	1.1	3.1	3.2	4.0
B3**	2.9	0.98	2.6	2.5	d	16.0	0.72	2.0	2.1	2.1
B4	3.0	1.1	2.4	2.8	d	26.0	0.72	2.0	2.0	2.8
B5	3.5	0.64	7.5	6.1	d	8.0	0.85	4.5	4.6	2.1
B6	1.9	0.81	1.9	1.5	0.38	d	0.45	1.5	1.5	2.1
B7**	2.3	1.2	3.8	3.7	d	16.0	0.97	3.5	3.3	2.7
B8**	2.3	0.92	2.3	2.1	0.41	d	0.49	1.7	1.9	2.1
Manure 1	0.43	0.021	d	d	d	d	d	d	d	d
Manure 2	0.75	d	d	d	d	d	d	d	d	d
d			0.080	0.15	0.04	0.15	0.06	0.05	0.09	0.2

(Continued)

- \* Nomenclature of PAHs given in Table 1.  
 \*\* Wetland stations.  
 † d = approximate detection limits.

Table 17 (Concluded)

Station	PAH Component*										
	11	12	13	14	15	16	17	18	19	20	21
A8	d†	1.1	3.0	1.7	3.8	0.67	1.3	3.4	3.0	0.81	1.1
A7	d	0.17	0.35	0.23	0.49	0.13	0.29	1.3	0.47	d	0.15
A6	d	0.15	0.43	0.25	0.56	0.14	0.43	0.29	0.47	d	0.13
A5	d	0.12	0.25	0.14	0.36	0.28	0.41	2.4	0.53	d	0.092
A4**	d	0.19	0.33	0.20	0.51	0.15	0.45	1.8	0.77	d	0.16
A3**	d	1.3	2.5	1.4	3.5	0.83	1.3	6.0	4.9	d	1.4
A2**	d	1.2	3.5	1.9	5.2	1.4	1.7	4.5	3.1	d	1.2
AlBl**	d	1.2	3.0	1.7	4.1	0.78	1.4	5.9	4.5	d	1.2
B2**	d	2.8	5.6	2.9	8.6	1.9	2.6	7.6	6.7	d	2.5
B3**	d	1.5	2.6	1.5	4.1	0.98	1.4	7.5	4.9	d	1.4
B4	d	1.7	3.0	1.7	4.5	1.0	1.5	7.9	5.4	d	1.5
B5	d	1.2	4.4	2.1	4.3	0.87	0.77	5.3	3.9	d	0.96
B6	d	1.3	2.3	1.2	3.6	0.97	1.8	3.7	2.9	d	1.1
B7**	d	1.6	4.0	2.2	5.3	1.1	1.7	7.8	5.6	d	1.6
B8**	d	1.4	2.4	1.4	3.6	1.1	1.6	3.9	3.1	d	1.2
Manure 1	d	d	d	0.032	d	d	d	0.80	d	d	d
Manure 2	d	d	d	d	d	d	d	d	d	d	d
d	1.0	0.01	0.025		0.02	0.1	0.09		0.1	0.025	0.02

\* Nomenclature of PAHs given in Table 1.

\*\* Wetland stations.

d = approximate detection limits.

Table 18  
PAH Concentrations ( $\mu\text{g}\cdot\text{g}^{-1}$  Ash-Free Dry Weight) in Experimental Worms  
Exposed to Times Beach Dredged Material in the Laboratory

Station	PAH Component*									
	1	2	3	4	5	6	7	8	9	10
A8	0.68	0.26	0.85	3.9	0.22	d†	0.49	1.2	1.0	1.5
A7	0.28	0.028	0.35	0.40	0.051	3.5	d	0.22	0.24	0.24
A6	0.091	0.0076	0.099	0.14	0.018	0.074	d	0.099	0.17	0.099
A5	0.18	0.011	0.070	0.11	d	0.16	d	0.086	0.16	0.21
A4**	0.20	0.011	0.071	0.14	0.032	0.23	d	0.098	0.17	0.20
A3**	0.36	0.047	0.12	0.23	0.18	1.0	d	0.25	0.43	1.9
A2**	0.28	0.062	0.41	0.53	0.11	1.6	0.17	0.17	0.41	0.75
A1B1**	1.4	0.37	2.4	4.5	0.13	12.0	0.77	1.7	1.7	3.1
B2**	0.57	0.066	0.19	d	0.51	3.6	0.68	0.35	0.47	4.2
B3**	0.36	0.063	0.20	0.27	0.18	2.3	0.11	0.25	0.53	2.5
B4	0.36	0.071	0.38	1.1	0.28	4.5	0.32	0.88	0.84	3.8
B5	0.25	0.010	d	d	0.045	0.72	d	0.093	0.18	0.91
B6	0.10	0.014	0.065	0.093	0.10	0.57	d	0.48	0.15	0.65
B7**	0.26	0.048	0.20	0.23	0.083	0.87	d	0.25	0.35	0.81
B8**	0.14	0.024	0.090	0.15	0.090	0.69	0.058	0.10	0.15	1.1
Manure	0.043	0.0016	0.12	d	d	0.021	d	0.16	d	d
d				0.015	0.0040	0.015			0.0085	0.02

(Continued)

\* Nomenclature of PAHs given in Table 1.

\*\* Wetlands stations.

† d = approximate detection limits.

Table 18 (Concluded)

Station	PAH Component*										
	11	12	13	14	15	16	17	18	19	20	21
A8	d†	0.41	2.1	1.3	2.8	0.71	0.58	1.5	1.3	d	0.14
A7	d	0.071	0.25	0.16	0.25	0.080	0.12	0.60	0.48	d	d
A6	d	0.043	0.15	0.11	0.16	0.050	0.076	0.19	0.21	d	0.0084
A5	d	0.036	0.16	0.10	0.14	0.061	0.11	0.60	0.30	d	d
A4**	d	0.055	0.22	0.12	0.25	0.11	0.15	0.50	0.44	0.013	0.011
A3**	d	0.44	1.5	0.62	2.1	0.36	0.68	1.5	2.2	0.017	0.13
A2**	d	0.37	1.3	0.65	1.8	0.32	0.43	1.1	1.1	d	0.11
A1B1**	d	0.93	5.2	2.7	5.8	0.60	0.97	1.8	4.4	d	0.28
B2**	d	1.8	5.4	2.6	7.4	0.73	1.4	3.2	5.0	d	0.60
B3**	d	0.61	2.3	1.0	2.9	0.42	0.79	1.7	3.1	d	0.13
B4	d	0.92	4.8	2.4	5.6	0.61	1.0	3.5	4.7	d	0.27
B5	d	0.27	0.64	0.30	0.75	0.24	0.36	0.89	1.3	d	0.032
B6	d	0.18	0.54	0.24	0.93	0.24	0.37	0.93	1.6	d	0.057
B7**	d	0.30	0.83	0.38	1.1	0.36	0.44	1.1	1.3	d	0.11
B8**	d	0.26	0.67	0.37	1.3	0.32	0.45	1.5	0.83	d	0.090
Manure	d	d	d	0.0047	d	d	d	0.160	0.029	d	d
d	0.1	0.0008	0.002		0.002	0.01	0.009			0.003	0.0025

\* Nomenclature of PAHs given in Table 1.

\*\* Wetlands stations.

† d = approximate detection limits.

54. Despite the higher concentrations of PAH components found in soils from the woodland section of the B transect compared with the A transect, worms exposed to these materials showed no substantial difference in concentrations in their tissues. As for the PCBs, rather high concentrations were found in worms exposed to wetland soils (A3 to B3) and Station B4.

55. The concentrations of many PAH components in native *Lumbricus terrestris* from Times Beach were 10 to 50 times as high as those from the reference site (Table 19). The concentrations in native worms at Times Beach did not differ greatly from those in the experimental laboratory worms, and regarding this comparability, the same remarks apply as for PCBs.

56. Tables 20 and 21 provide the concentrations of PAH components in fishes from Times Beach and the aquatic reference area. Known mutagens were below detection limits or only occasionally detected in very low concentrations. The concentrations of the components that could be quantified appeared to be about 5 to 10 times higher in fishes from Times Beach than in those from the reference site. The carp collected from Times Beach also contained higher levels of phenanthrene and substantially lower levels of benzo(a)anthracene and benzo(a)pyrene than were reported previously for carp collected in the Buffalo River (Black, Dymerski, and Zapisek 1981).

#### Field Experimental Worms

57. The previous discussions regarding experimental worms were the results of bioassays conducted under controlled conditions in an environmental chamber using field-collected dredged materials. As reported herein, worms were also exposed in the field at all stations where materials were collected for the laboratory experiment. The following discussion is based upon earthworm studies conducted in the field at Times Beach. The concentrations of heavy metals, PCBs, HCB, and PAHs in these worm samples are shown in Tables 22 and 23.

58. As indicated in Table 2, a large variation was encountered in the weights of the control worms. A similar, rather large, variation was also found in the contaminant levels of these control worms. This may account for some of the variation in the heavy metals (e.g., Cd) and some of the PAH components. Moreover, the levels of contaminants in the control worms from the field experiment were sometimes much higher than in the control worms from the

Table 19

PAH Concentrations ( $\mu\text{g}\cdot\text{g}^{-1}$  Ash-Free Dry Weight) in Native Worms  
at Time Beach and a Reference Area

Area	Species	PAH Component*									
		1	2	3	4	5	6	7	8	9	10
T.B.	<i>A. rubellus</i>	0.36	0.13	0.62	0.37	0.013	0.94	0.13	0.53	0.48	0.32
		0.20	0.059	0.24	0.17	0.014	0.56	0.038	0.22	0.23	0.23
Ref.	<i>A. rubellus</i>	0.11	0.0048	0.051	d**	d	d	d	0.012	0.020	d
		0.17	0.0090	0.086	d	d	d	d	0.022	0.040	d
	<i>A. chlorotica</i>	0.20	0.0064	0.090	d	0.0071	0.045	d	0.012	d	d
		0.13	0.0042	0.066	d	d	0.023	d	0.0070	0.014	d
	<i>A. lacteum</i>	0.088	0.0040	0.039	d	0.0040	0.013	d	0.0074	d	d
		0.11	0.0051	0.057	d	d	0.020	d	0.0072	0.027	d
d					0.002	0.0055	0.02	0.01		0.01	0.0035
T.B.	<i>A. rubellus</i>	d**	0.19	0.45	0.27	0.59	0.16	0.15	0.76	0.48	0.14
		d	0.13	0.27	0.14	0.31	0.086	0.13	0.64	0.30	0.086
Ref.	<i>A. rubellus</i>	d	0.0048	0.024	0.010	0.011	d	d	0.10	d	d
		d	0.0027	0.034	0.015	0.018	d	d	0.14	d	d
	<i>A. chlorotica</i>	d	d	0.0083	0.0051	d	d	d	0.17	d	d
		d	d	0.0085	0.0049	0.0028	d	d	0.18	d	d
	<i>A. lacteum</i>	d	d	0.0074	0.0047	d	d	d	0.14	d	d
		d	0.0015	0.019	0.0080	0.0065	d	d	0.13	d	d
d		0.15	0.0015			0.003	0.015	0.015	0.015	0.004	0.003

\* Nomenclature of PAHs given in Table 1.

\*\* d = approximate detection limits.

Table 20

PAH Concentrations ( $\mu\text{g}\cdot\text{g}^{-1}$  Ash-Free Dry Weight) in Fishes at Times Beach and the Adjacent Mouth of the Buffalo River

Area	Species**	Organ	PAH Component*									
			1	2	3	4	5	6	7	8	9	10
T.B.	Y.P.	muscle	0.071	0.023	0.024	d	0.0051	0.056	d†	d	d	d
		liver	0.77	0.26	0.25	0.19	0.042	0.58	d	0.015	d	d
	P.S.	muscle	0.11	0.044	0.065	0.025	d	0.16	d	d	d	d
		liver	0.53	0.16	0.33	0.11	0.017	0.95	d	d	d	d
	R.B.	muscle	0.12	0.018	0.031	d	d	d	d	d	d	d
		liver	0.45	0.17	0.20	0.08	d	d	d	d	d	d
	C.	muscle	0.39	0.095	0.095	0.16	d	d	d	d	d	d
		liver	0.63	0.20	0.16	0.20	d	d	d	d	d	d
B.R.	Y.P.	muscle	0.036	0.0025	0.0066	d	d	d	d	d	d	d
		liver	0.11	0.022	0.045	0.069	0.013	0.026	d	d	d	d
	P.S.	muscle	0.031	0.0022	0.0012	d	d	d	d	d	d	d
		liver	0.059	0.0070	0.037	0.051	0.0070	d	d	d	d	d
d† d		muscle				0.02	0.003	0.01	0.008	0.007	0.01	0.03
		liver						0.02	0.02	0.01	0.03	0.08

(Continued)

\* Nomenclature of PAHs given in Table 1.

\*\* Y.P. = yellow perch; P.S. = pumpkinseed; R.B. = rock bass; C = carp.

† d = approximate detection limits.

Table 20 (Concluded)

Area	Species**	Organ	PAH Component*										
			11	12	13	14	15	16	17	18	19	20	21
T.B.	Y.P.	muscle	d†	d	d	0.0041	d	d	d	0.15	d	d	d
		liver	d	0.070	d	0.011	d	d	d	0.55	d	d	d
	P.S.	muscle	d	d	d	0.0027	d	d	d	0.13	d	d	d
		liver	d	d	0.0095	0.014	d	d	d	0.63	0.13	d	d
	R.B.	muscle	d	d	d	0.0055	d	d	d	d	d	d	d
		liver	d	d	d	0.0067	d	d	d	d	d	d	d
	C.	muscle	d	0.012	0.036	d	d	d	d	d	d	d	d
		liver	d	d	d	0.0059	d	d	d	d	d	d	d
B.R.	Y.P.	muscle	d	d	d	0.0030	d	d	d	0.14	d	d	d
		liver	d	0.0075	d	0.0015	d	d	d	0.047	0.0084	d	d
	P.S.	muscle	d	d	d	0.0033	d	d	d	0.15	d	d	d
		liver	d	d	d	0.0048	d	d	d	0.22	d	d	d
d		muscle	0.1	0.0015	0.003		0.0025	0.01	0.01		0.0035	0.003	
d		liver	0.35	0.0035	0.0009		0.007	0.040	0.03		0.0015	0.0095	0.008

† d = approximate detection limits.

Table 21

PAH Concentrations ( $\mu\text{g}\cdot\text{g}^{-1}$  Fresh Weight) in Fishes at Times Beach and the Adjacent Mouth of theBuffalo River

Area	Species**	Organ	PAH Component*									
			1	2	3	4	5	6	7	8	9	10
T.R.	Y.P.	muscle	0.014	0.005	0.005	d†	0.001	0.011	d	d	d	d
		liver	0.437	0.147	0.142	0.108	0.024	0.329	d	0.009	d	d
	P.S.	muscle	0.02	0.008	0.012	0.005	d	0.030	d	d	d	d
		liver	0.101	0.03	0.063	0.021	0.003	0.181	d	d	d	d
	R.B.	muscle	0.024	0.004	0.006	d	d	d	d	d	d	d
		liver	0.080	0.030	0.036	0.014	d	d	d	d	d	d
	C.	muscle	0.078	0.019	0.019	0.032	d	d	d	d	d	d
		liver	0.161	0.051	0.041	0.051	d	d	d	d	d	d
B.R.	Y.P.	muscle	0.007	0.0005	0.0013	d	d	d	d	d	d	d
		liver	0.059	0.012	0.024	0.037	0.007	0.014	d	d	d	d
	P.S.	muscle	0.006	0.0040	0.0002	d	d	d	d	d	d	d
		liver	0.011	0.0013	0.007	0.010	0.0013	d	d	d	d	d

(Continued)

\* Nomenclature of PAHs given in Table 1.

\*\* Y.P. = yellow perch; P.S. = pumpkinseed; R.B. = rock bass; C = carp.

† d = approximate detection limits.

Table 21 (Concluded)

Area	Species**	Organ	PAH Component*										
			11	12	13	14	15	16	17	18	19	20	21
T.B.	Y.P.	muscle	d†	d	d	0.0008	d	d	d	0.030	d	d	d
		liver	d	0.040	d	0.006	d	d	d	0.312	d	d	d
	P.S.	muscle	d	d	d	0.0005	d	d	d	0.024	d	d	d
		liver	d	d	0.0018	0.003	d	d	d	0.119	0.025	d	d
	R.B.	muscle	d	d	d	0.0011	d	d	d	d	d	d	d
		liver	d	d	d	0.0012	d	d	d	d	d	d	d
	C.	muscle	d	0.002	0.007	d	d	d	d	d	d	d	d
		liver	d	d	d	0.0015	d	d	d	d	d	d	d
B.R.	Y.P.	muscle	d	d	d	0.0006	d	d	d	0.028	d	d	d
		liver	d	0.0040	d	0.0008	d	d	d	0.025	0.0045	d	d
	P.S.	muscle	d	d	d	0.0006	d	d	d	0.027	d	d	d
		liver	d	d	d	0.0009	d	d	d	0.041	d	d	d

† d = approximate detection limits.

Table 22

## Heavy Metals, PCB, and HCB in Experimental Worms Exposed Under Field Conditions

Station	Heavy Metals*				PCB Isomers**										HCB
	Cd	Cu	Hg	As	28	52	49	70	101	87	153	138	180		
Times Beach															
A8	17.7	28.8	1.34	33.3	49	290	180	530	270	110	210	250	100	260	
A7					390	1,300	940	1,800	680	330	340	310	88	710	
A6	16.6	37.2	1.45	34.9											
A5															
A4†	8.96	28.7	1.16	21.5	220	750	540	1,000	360	160	150	190	64	310	
A3†	18.1	40.3	0.92	21.6											
A2†					170	860	550	1,300	600	280	320	470	120	780	
A1B1†															
B2†															
B3†					340	2,200	1,600	2,200	1,100	560	410	720	140	370	
B4					100	1,300	770	1,600	870	430	370	530	120	1,100	
B5															
B6															
B7†															
B8†	17.7	47.1	1.63	37.3											
Manure Controls															
A7	11.3	14.7	0.080	44.8	25	-	18	30	12	-	-	-	9.8	7.1	
A5															
A3†	5.56	14.4	0.054	37.8	39	24	16	35	14	-	15	23	10	17	
A1B1†															
B2†	2.30	12.7	0.039	38.3	24	23	16	44	17	-	-	25	11	87	
	2.77	13.1	-	41.5											
B4															
B6															
B8†	4.29	8.51	0.047	15.4	24	24	19	39	24	8.8	34	100	15	21	

\*  $\mu\text{g}\cdot\text{g}^{-1}$  ash-free dry weight.\*\*  $\mu\text{g}\cdot\text{kg}^{-1}$  ash-free dry weight; nomenclature of PCBs given in Table 1.

† Wetland stations.

Table 23  
PAH Components in Experimental Worms Exposed Under Field Conditions\*

Station	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	PAH Components**																				
Times Beach																					
A8	0.46	0.025	0.14	0.15	0.043	0.57	d††	0.11	0.19	0.35	d	0.16	0.40	0.24	0.43	0.18	0.32	1.0	1.0	0.015	0.058
A7																					
A6	3.1	0.16	1.2	0.92	0.092	0.36	d	0.30	0.28	0.58	d	0.12	0.46	0.28	0.33	0.16	0.30	d	0.82	d	d
A5	0.54	0.017	0.12	0.21	0.14	0.78	0.083	0.18	0.23	1.7	d	0.52	1.8	0.73	2.1	0.48	0.92	2.3	2.8	d	0.13
A4†																					
A3†	1.1	0.045	0.26	0.29	0.057	0.56	0.049	0.18	0.23	0.59	d	0.15	0.54	0.28	0.51	0.18	0.33	0.70	0.81	d	0.033
A2†																					
AlB1†																					
B2†																					
B3†																					
B4	0.59	0.027	0.13	0.40	0.26	1.38	0.26	0.44	0.45	2.83	d	0.78	2.59	1.20	3.9	0.61	0.82	2.2	2.9	d	0.23
B5																					
B6																					
B7†																					
Manure Controls																					
A7	0.30	0.0098	0.11	0.13	d	d	d	0.027	0.069	d	d	d	0.017	0.017	0.011	d	d	d	d	d	d
A5																					
A3†	0.28	0.0088	0.10	0.11	d	d	d	0.029	0.054	d	d	0.0056	0.017	0.016	0.015	d	d	d	d	d	d
AlB1†																					
B2†	0.32	0.0095	0.19	0.21	d	0.18	d	0.043	0.070	d	d	d	0.021	0.020	0.012	d	d	d	d	d	d
B3†	0.31	0.0087	0.18	0.20	0.020	0.17	d	0.045	0.064	d	d	d	0.018	0.020	0.012	d	d	d	d	d	d
B4																					
B6																					
R8†	0.32	0.011	0.14	0.17	d	d	d	0.033	0.067	d	d	d	0.018	0.018	0.019	d	d	d	d	d	d

\* ug/g ash-free dry weight.

\*\* Nomenclature of PCBs given in Table 1.

† Wetland stations.

†† d = approximate detection limits.

environmental chamber experiment. The real reason for this difference is unknown, although contaminant movement from surrounding soils during flooding and also washing of surface contaminants from the leaf canopy by rainfall passing through the tree canopy might be suspected.

59. When a comparison is made station by station between the field and laboratory, it becomes obvious that the results differ less than one order of magnitude, a difference that may be explained in part by variations in the controls. Most of these differences are probably the result of fluctuation in exposure conditions (such as temperature or moisture) in the field when compared with the relative stability of conditions in the environmental chamber.

## PART IV: CONCLUSIONS

### Heavy Metals

60. Compared with the terrestrial reference site, the concentrations of heavy metals in the only native worm species collected at Times Beach are increased 2 to 5 times.

61. The concentrations of Cd in these native Time Beach worms are somewhat elevated in relation to available data concerning Cd in worms. These elevated Cd concentrations might be due to enrichment of the forest floor by Cd through yearly leaf fall, as indicated from the soil analysis of different layers. Indications also were found that other metals may become similarly enriched in the surface layer.

62. In the wetland area, the survival potential for experimental worms proved to be very poor. No native worms were found in that area, probably because of occasional flooding.

63. With the exception of Hg, no indications were found for elevated levels of heavy metals in fish from Times Beach in relation to the selected aquatic reference site. Hg in edible tissues of fish from Times Beach was slightly below the FDA limit of  $1\text{-}\mu\text{g}\cdot\text{g}^{-1}$  wet weight allowed in fish for human consumption.

64. For the site as a whole, two potential metal accumulation problems were associated with the faunal elements:

- a. Hg in the fish from Times Beach (~50 percent of the total area).
- b. Cd in the worms from the woodland portion (~25 percent of the total area).

65. In relation to possible effects on food chains (e.g., birds and game), it appears that both of the above subareas of Times Beach are too small for total lifetime exposure of birds and mammals in either habitat, leading to low risks. There is a need to further quantify movement of heavy metals through existing food webs at the site.

66. Because the Hg levels in yellow perch at Times Beach approach FDA limits, extensive consumption of fish caught in this area should probably be avoided.

67. The elevated concentrations of Cd and related contaminants in the woodland area might be handled through managing plant life (trees). Further information about actual contaminant concentrations in the leaves and the plant biomass is essential in the further formulation of a management strategy.

#### PCB Components and HCB

68. Compared with the terrestrial reference site, concentrations of PCB components and HCB in the native worm species at Times Beach were increased at least 10- to 20-fold.

69. The experimental worms exposed in the laboratory to materials from the woodland accumulated PCB and HCB to levels comparable with those of native worms.

70. Very high concentrations were found in the experimental worms exposed in the laboratory to materials from the wetland, where no native worms occur naturally.

71. Concentrations of PCBs and HCB in fishes from Times Beach were elevated above those from the aquatic reference site. The total of the nine PCB congeners analyzed was considerably less than the FDA limit of  $2\text{-}\mu\text{g}\cdot\text{g}^{-1}$  fresh weight in edible tissues of any species caught at Times Beach. The PCBs analyzed may have represented only a small fraction of the total PCB present, with the potential consequence that the total PCB present in the edible tissues may possibly have exceeded the  $2\text{-}\mu\text{g}\cdot\text{g}^{-1}$  FDA limit.

72. Consequently, it is recommended that fishes caught at Times Beach should not be eaten unless further studies can demonstrate conclusively that no problem exists for human health.

73. A potential management strategy might consist of underwater capping to such an extent that about 0.50 m of water is maintained. In this way, the game fish population will be reduced with minimal adverse impact upon the Times Beach site as a whole.

#### PAH Components

74. Rather high concentrations ( $>3$  to  $5\text{ }\mu\text{g}\cdot\text{g}^{-1}$ ) of some PAH components were found in dredged materials at Times Beach.

75. The ratios among the components change to a very large extent with soil depth. Weathering over the past 7 years and biological activity are thought to be the cause.

76. The experimental worms showed a high potential for uptake when exposed in the laboratory to materials from the wetland.

77. Experimental worms exposed in the laboratory to materials from areas of the transect in the woodland accumulated concentrations similar to those found in native worms on the site.

78. Concentrations of PAH components in native worms from Times Beach were 10 to 50 times as high as in the same species from a reference site.

79. Fish species from Times Beach contained PAH concentrations 5 to 10 times higher than those in fish from an aquatic reference site. Known mutagens were less than detection limits or were only occasionally detected in low concentrations.

80. For the site as a whole, PAH accumulation by earthworms in the laboratory was greatest in the wetland. This suggested that bioaccumulation of PAH by invertebrates living in the wetland sediments could be potentially substantial. Although generally lower PAH concentrations were found in experimental worms from the woodland area, the concentrations of some known mutagens were still relatively high. Further studies should focus on the fate of the most persistent of the PAHs in the food webs.

#### Field Experimental Worms

81. In the field experiment, a wide variation was observed in the final tissue weights and in the concentrations of heavy metals and some PAHs in worms exposed to the control substrates. This variation is probably a reflection of the differences in physical conditions along the transect, such as flooding, rainfall, and temperature.

82. The field experiment indicated that *E. foetida* could survive in the upland dredged materials at Times Beach for a period of at least 22 days under the prevalent climatic conditions. Worms did not survive in the wetland under field exposure conditions because of flooding.

83. The results of earthworm tests conducted in the field were extremely variable because of many uncontrollable environmental factors (e.g., flooding, wide fluctuations in temperature, and drought). The effects of

these environmental factors apparently were compounded by the restrictive caging procedure used in this preliminary assessment, with the consequence that periodic flooding, extreme overheating, and occasional total desiccation of the soil within the cages resulted in loss of test animals. A less restrictive procedure that allows the worms to migrate away from occasionally flooded soils or to burrow deeper in response to heat or desiccation is needed to ensure adequate recovery of animals used in field biomonitoring situations.

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